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SOIL SCIENCE

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STUDIES ON SOIL PROTOZOA

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ANNUAL CYCLE OF SOIL PROTOZOA OF A POOR JERUSALEM SOIL

The observations were conducted in a wheat field on the western decline of Mount Scopus, near Jerusalem. The field was very shallow and had been worked primitively, without any manuring. The soil is described by Dr. A. Reifenberg as follows: "A yellow-brown, loamy lime-soil, which contains in considerable numbers undecomposed limestone fragments. The fine earth (particularly below 2 mm. diameter) contains 55.5 per cent $CaCO_3$. Its lime content is exceptionally high. The reaction of the soil is alkaline (pH = 7.5: colorimetric measurement). The soil contains dry plant remains, but no humus."

The technique of the present study was as follows: The soil was taken from the upper 5 cm., well mixed, and treated according to the method of Cutler (2) (dilution, cultivation in bouillon-agar, and hay infusion, etc.). The number of cysts was calculated by determining the difference between untreated soil and soil washed with 2 per cent HCl. The soil proved to be extremely poor in species of soil protozoa. The full list is (4):

Ciliata: *Colpoda steinii* Maup.

Flagellata: *Cercobodo* sp.
Heteromita globosa Stein
Pleuromonas jaculans Perty
Cercomonas longicauda Stein

Rhizopoda: *Mayorella palestinensis* Reich
Microamoeba oblonga Reich
3 *Amoebae* spp. of the *limax*-group
Amoeba sp. of the *proteus*-group

Sandon (6), who has studied the species of six different Palestine soils, obtained an average of 13.8 (8–31) species per soil. Our soil contained an average of 12.3 species. It should be noted, however, that two of our species occurred only very occasionally and that Sandon has studied only one sample of each soil. The distribution of the different groups, if we use the correction

factor set by Sandon (1.1 for Flagellata, 1.3 for Ciliata, 1.1 for Amoeba, 1.7 for testaceous Rhizopoda) is:

	CILIATA	FLAGELLATA	AMOEBA	TEST. RHIZOPODA	TOTAL
Sandon's average	3.7	6.4	2.4	0.6	13.1
Our Jerusalem soil	1.3	4.4	6.6	0.0	12.3
Difference	−2.4	−2.0	+4.2	−0.6	−0.8

But the average of the Palestine soils studied by Sandon was much influenced by the richness of his sample 8. The following is our comparison:

	CILIATA	FLAGELLATA	AMOEBA	TEST. RHIZOPODA
Best soil No. 8	6.7	14.3	6.0	3.6
Average of 5 other soils	3.3	4.8	1.7	0
Average of 3 poorest soils	1.9	4.2	1.8	0
Jerusalem soil	1.3	4.4	6.6	0

The differences as compared with our soil are relatively small. The number of Ciliata would have changed considerably had one other species only (as *C. cucullus* or *Oxytricha*) been present. The much higher standard with regard to *Amoeba* certainly constitutes no real difference, but is based on the fact that Sandon did not distinguish his species as well as we did, especially with regard to the *Amoeba limax* group. The annual fluctuation of the nine species, which appeared more or less regularly in the soil, is denoted in table 1.

The maximal active development for these species is:

	NOVEMBER	DECEMBER	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER
Number of species at maxima	1	1	....	3	3	3	1	....	....	....	....	....
Per cent soil humidity (difference between fresh and dry soil)	12.2	7.1	12.1	11.1	11.8	12.3	4.3	4.3	1.5	2.2	1.0	2.2

It is obvious, therefore, that the winter rains start a period of activity, but only after a protracted period of soil saturation, and the rise of soil temperature in February induces the peak of this activity.

SOURCES OF ERROR IN PRESENT METHODS OF DETERMINING THE NUMBER OF CYSTS

When we compare the number of active stages and of cysts in table 1, we are confronted by the startling fact that, except in two instances, *Mayorella*

TABLE 1

Number of active protozoa (a) and of cysts (b) for every month of the year per gram of the soil (dry weight)

		NOVEMBER 23, 1930	DECEMBER 5, 1930	JANUARY 6, 1931	FEBRUARY 5, 1931	MARCH 9, 1931	APRIL 13, 1931	MAY 3, 1931	JUNE 14, 1931	JULY 14, 1931	AUGUST 17, 1931	SEPTEMBER 19, 1931	OCTOBER 10, 1931
1. *Cercobodo* sp.	a	182	253	182	504	2034	730	166	82	282	112	323	459
	b	90	121	17	28	28	29	39	16	7	7	....	....
2. *Heteromita globosa*	a	90	495	262	717	362	513	39	114	232	112	162	235
	b	63	42	7	....	28	17	....	7	....	....	....	....
3. *Pleuromonas jaculans*	a	365	28	43	42	42	43	26	....	....	....	25	....
	b	7	17	....	....	....	7	....	....	....	....	....	....
4. *Cercomonas longicauda*	a	17	62	63	123	124	63	....	7	15	38	38	15
	b	17	28	17	28	7	7	7	....	....	....	....	....
5. *Mayorella palestinensis*	a	....	....	....	....	....	17	....	....	....	7	7	....
	b	17	352	262	717	42	17	39	....	111	80	7	235
6. *Microamoeba oblonga*	a	....	....	....	123	63	125	7	16	7	26	15	15
	b	....	....	....	62	16	....	....	....	....	7	....	....
7. *Amoeba* No. 2	a	....	....	....	....	....	7	....	....	....	....	....	....
	b	....	....	....	7	....	7	....	....	....	....	....	....
8. *Amoeba* No. 4	a	7	42	17	7	....	17	16	16	7	7	7	15
	b	....	....	....	....	....	....	....	....	....	....	....	....
9. *Amoeba x*	a	....	....	....	28	7	29	7	....	....	15	15	....
	b	....	....	....	....	7	....	....	....	....	....	....	....

palestinensis has more cysts than active forms. Our method was that actually used and proposed by Cutler (2). The soil is exposed to the influence of a 2 per cent solution of HCl overnight. It is supposed that at the end of this exposure, all active stages are dead, but no cysts damaged. This supposition is certainly not true, as the following experiments will show:

TREATMENT OF CULTURE	NUMBER OF INDIVIDUALS SURVIVING TREATMENT
1. Cercomonas longicauda	
I. Untreated control	15,200
II. 1.10 per cent HCl at 21°C	.....
III. 1.4 per cent HCl at 21°C	.....
IV. 1.8 per cent HCl at 21°C	.....
V. 2.0 per cent HCl at 21°C	.....
2. Cercomonas longicauda	
I. Untreated Control	72,000
II. 2 per cent HCl at 10°C	220
III. 2 per cent HCl at 16°C	76
IV. 2 per cent HCl at 22°C	50
3. Cercobodo sp.	
I. Untreated control	2,600
II. HCl 2 per cent at 11°C	.....
III. HCl 2 per cent at 15°C	.....
IV. HCl 2 per cent at 22°C	.....
4. Mayorella palestinensis Reich.	
I. HCl 2 per cent at 9.5°C	30,000
II. HCl 2 per cent at 16°C	15,000
III. HCl 2 per cent at 22°C	640

5. Soil sample

TREATMENT	NUMBER OF INDIVIDUALS SURVIVING				
	Cercobodo sp.	*Cercomonas longicauda*	*Heteromita globosa*	*Mayorella palestinensis*	*Amoeba* sp.
I. Untreated Control	1,300	38	1,800	6.8	167
II. HCl 2 per cent at 10°C	79	..	56	56	7
III. HCl 2 per cent at 24°C	56	..	38	15	..

It becomes obvious that the cysts of at least some of the soil protozoa become decidedly damaged by the treatment with HCl. The degree of this damage depends largely upon the prevailing environmental temperature, as is demonstrated in experiments 2 and 4. The value and applicability of the HCl method are thereby much restricted, and at higher temperatures the method is probably altogether valueless. Other methods (except the direct count) were unknown up to date, and we believe it impossible to draw from the relation between the numbers in active stages and the cysts (table 1) any conclusions whatsoever on the annual activity of the protozoa observed. With regard

to the very strange behavior of *Mayorella palestinensis*, we are not yet able to make a statement as to whether it is produced by direct stimulation of the cysts as a result of treatment with HCl, or whether it is attributable to the extermination of the bacteria in the culture medium (which have in other protozoa a well-known stimulative effect).

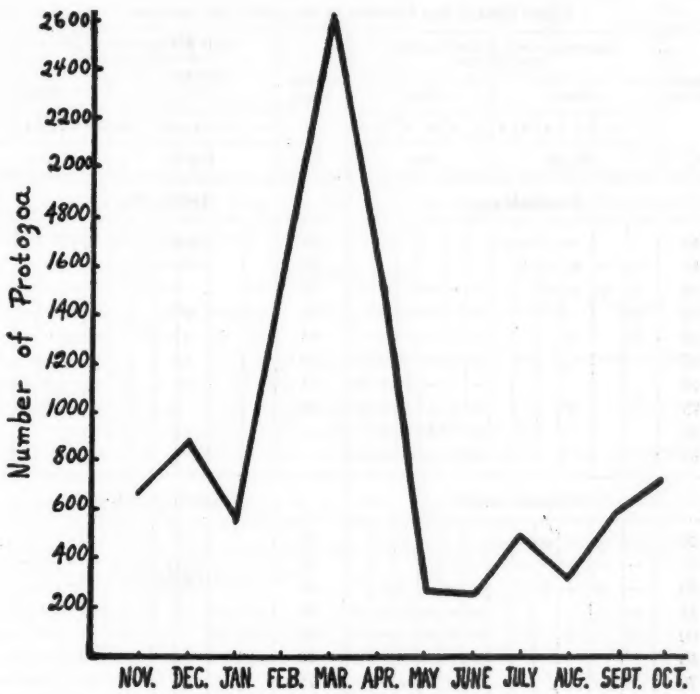

FIG. 1. NUMBER OF SOIL PROTOZOA

Sum of all individuals of all species during the year

UPPER LIMIT OF HEAT TOLERANCE IN THE CYSTS OF SOIL PROTOZOA

Some indications of the upper limit of heat tolerance in the cysts of soil protozoa (after exposure of 1 hour) may be found in the literature:

COUNTRY	AMOEBA	CILIATA	FLAGELLATA
	°C.	°C.	°C.
A. Egypt (3)	75–80	71–73	75–80
B. England (1)	72	72	70–72
C. England (5)	..	56	...

In samples A and B dry soil was tested, in sample C cysts from artificial cultures. Our own experiments explain this difference easily. Cysts in moist soil (our humid series) show a much lower tolerance than those from soil which was air-dried for more than 2 months.

TABLE 2

Upper limit of heat tolerance in the cysts of soil protozoa

TEMPERATURE	PROTOZOA ALIVE OR DEAD* AFTER EXPOSURE OF											
	Hours						Hours					
	1	2	3	4	5	6	1	2	3	4	5	6
°C.	Humid						Dry					
	Cercobodo sp.											
40			−	−	−	−						
45	−	−	+	+	+							
50	+	+	+	+			−	−	−	−	−	−
55	+						−	−	−	−	−	−
60	+		+				−	−	−	−	−	−
65							−	−	−	−	−	−
70							−	−	−	+	+	+
75			+				−	+	+	+	+	+
80							+	+	+	+	+	+
85							+	+	+	+	+	+
	Colpoda steinii											
40	−	−	−	−	−	−						
45	−	−	−	−	−	−						
50	−	+	+	+			−	−	−	−	−	−
55	−						−	−	−	−	−	−
60	+		+				−	−	−	−	−	−
65							−	−	−	−	−	−
70							−	−	−	−	−	−
75			+				−	−	+	+	+	+
80							+	+	+	+	+	+
85							+	+	+	+	+	+

TEMPERATURE	PROTOZOA ALIVE OR DEAD* AFTER EXPOSURE OF											
	Hours						Hours					
	1	2	3	4	5	6	1	2	3	4	5	6
°C.	Humid						Dry					
	Amoeba No. 2											
45						−						
50			−	−	−	−	−	−	−	−	−	−
55	−		−	−	+		−	−	−	−	−	−
60	−	−	+				−	−	−	−	−	−
65	+	+					−	−	−	−	−	−
70							−	−	−	−	−	−
75			+				−	−	+	+	+	+
80							+	+	+	+	+	+
	Mayorella palestinensis											
45						−						
50			−	−	−	−	−	−	−	−	−	−
55	−		+	+	+		−	−	−	−	−	−
60	−	−	−				−	−	−	−	−	−
65	+	+					−	−	−	−	−	−
70	+						−	−	−	−	−	−
75			+				−	−	−	−	−	−
80							−	+	+	+	+	+
90							+	+	+	+	+	+

* − = living; + = dead.

These results may be summed up as follows:

	UPPER HEAT TOLERANCE OF CYSTS IN	
	Humid Series	Dry Series
	°C.	°C.
Cercobodo sp.	50	80
Colpoda steinii	60	80
Mayorella palestinensis	65	85*
Amoeba No. 2	65	80

* Approximately.

This means that cysts may also show under different environmental conditions an entirely different tolerance for heat; the degree of dehydration of the cysts is especially important in this respect.

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PROFILE STUDIES OF THE COASTAL PRAIRIE SOILS OF LOUISIANA: I. EXCHANGE AND SOLUTION PROPERTIES[1]

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Received for publication October 16, 1933

The Coastal Prairie Area of southwest Louisiana and southeast Texas offers many unique problems for solution. Although some areas in this region have been mapped and the soils classified, no extensive laboratory investigations of these soils have been previously undertaken. This paper is the first of a series of studies of the morphology and genesis of the soils of this area and the effects produced upon the chemical, physical, and biological properties by current methods of agricultural practices.

In Louisiana the Coastal Prairie Area is situated in the extreme southwest corner of the state and extends northward from the Gulf of Mexico for a distance of 80 miles. It extends eastward from the Texas border about 125 miles. The area is small in comparison with the total area of the state, yet economically it is very important.

The soils of this area are relatively young, since the area only recently emerged from the Gulf of Mexico; the upper geological strata belong to the Port Hudson group of the Columbian Quarternary (6, 7). However, this does not mean that well-developed profiles are not in evidence, since sufficient time has elapsed for soil forming processes to cause such development. Natural drainage channels are poorly developed, and in conjunction with the flat topography and low elevation drainage is poor throughout the area. The rainfall is relatively high, averaging 53 inches per year, and the average temperature is likewise high, 68°F., with only a few killing frosts occurring in any year. The natural vegetation is grasses, although along the eastern and northern boundaries a transition belt of forest occurs. Because of the high rainfall, flat topography, and slow percolation of water through these soils, the cultivation of rice as the main agricultural crop has been developed. This crop, because of the irrigation or flooding of the soil required for its growth, has caused marked changes in the soil.

A study of these soils in the field has shown that the cultivation of rice has increased the stickyness, compactness, and imperviousness to the passage of water through the soil. At the present time the mechanism of these changes

[1] Published with the permission of the director of the Louisiana Agricultural Experiment Station and the dean of the College of Pure and Applied Science.

[2] Associate professor of chemistry and assistant soil technologist respectively.

in physical conditions of the soil is not entirely clear. It may be postulated that all of the following changes are instrumental in bringing this about:

1. Increased hydrolysis due to prolonged flooding with the liberation or solution of sodium ions, which have produced a partial sodium soil with the resultant change in physical properties.
2. Introduction of relatively high amounts of sodium ions in comparison with calcium and magnesium ions through the irrigating water, producing a condition similar to that resulting from such a case as the foregoing.
3. An increase in the dispersable colloid content of the soil due either to the direct effects of large amounts of water on the hydrolysis of the mineral content of the soil or to acceleration of hydrolysis by the ions present in solution.
4. The production of a highly reducing condition with the resultant solution and carrying to lower horizons of various elements, particularly iron and manganese.

All of these four factors will cause a change in the physical properties of the soil, in each case increasing the compactness and impermeability. The fate

TABLE 1

Analyses of water (6)

	LAKE CHARLES ARTESIAN WELL	INDIAN BAYOU	ENGLISH BAYOU
	p.p.m.	*p.p.m.*	*p.p.m.*
Calcium	21.0	15.0	11.0
Magnesium	8.0	11.0	3.0
Sodium	54.0	61.1	12.0
Potassium	30.0	30.0	6.0
Sulfate	10.0	26.0	4.0
Chloride	46.0	140.0	24.0
Bicarbonate	189.0	30.0	42.0

of the soil due to the introduction of sodium ions into the exchange complex will be similar to that taking place in arid regions, but will be less drastic, because of the lower concentration of the sodium ions present. Under the conditions that occur in Louisiana, where we have alternate years of flooding and fallow or cultivated crops, a high rainfall, and small quantities of sodium ions in the irrigating water, the saline or solonchak stage is transitory and would undoubtedly be in evidence only immediately after the removal of the saline irrigating water. In table 1 are given data on the analysis of water as reported by Heileman and Mesmer (7). During periods of drought, waters containing much higher amounts of soluble salts are sometimes used. Rice (12) reports such a condition for the summer of 1902 when great damage resulted from this cause. During such periods, when excessive quantities of water are used, the level of the water in the natural streams and bayous may become so low that saline waters from the Gulf of Mexico may back up to considerable distances and result in their becoming too saline for use on rice lands. As a result of the recurring saline conditions a weakly developed solonetz stage tends to be

formed. Dr. C. C. Nikiforoff states:[3] "Besides the typical solonetz there is a great group of soils alkalized to a lesser degree. The outstanding features of these soils are: chemical, some proportion of exchangeable sodium but relatively small; physical and morphological, compactness of the alkalized or solonized section of the profile. Such soils are much more common than the typical solonetz. They possess all the properties of the solonetz but in a smaller degree." There is associated with the effect of a lesser salinized condition upon the physical and chemical properties, the effect of restricted percolation which hinders the removal of the products of silicate weathering. As a consequence the weathering complex is more siliceous than where drainage is better (13). The accumulation of siliceous material and the existence of reducing conditions account for the gray colors and the pockets, stringers, or tongues of ashy degraded material in these soils. This is very much in evidence where a comparison is made between flooded and virgin soils. In all cases the irrigated soils show a much greater development of ashy siliceous material, and its occurrence is one of their outstanding characteristics.

The soil development in this region has taken place under rather sharply varying conditions The rainfall has been too high to permit the formation of a typical solonetz profile. Yet the original materials which contained calcareous shells, in passing through the tidal or saline marsh to the fresh water marsh and then to the low upland prairie with the recurrence from time to time of both natural and artificial floodings with saline waters, have left some profiles which in their older development are acid throughout, others which are younger or contained in the beginning more calcareous material and are acid only in the A horizon, and a few that do not occur widely, which are definitely alkaline. The movement of a great amount of rainfall as sheet water from the surface is a very important factor in the removal of salts from the soil. Following the emergence of the soil material from brackish water there was the rapid removal of soluble salts due to the heavy rainfall. Then, with the succession of grass flora, the occurrence of a definite alkaline stage was only transitory because of intense weathering by carbonation and hydrolysis associated with the quick removal of the soluble products from the surface horizon. This undoubtedly accounts for the ashy accumulations of siliceous pockets and tongues. The surface of the virgin soils are finely granular as a result of the relatively high accumulation of humus under grassland conditions, but under cropping and alternate flooding from irrigation, which causes the loss of organic matter, the soil becomes deflocculated. If at any time the irrigation waters contain salts there is a tendency toward a redevelopment of the alkaline stage which may be unnoticeable or very apparent depending upon the number of floodings and the concentration of salts in the water.

EXPERIMENTAL

Of the soils used in this study, two are from virgin fields and presumably have never been flooded; namely, soils 2 and 3; two have been flooded only with deep

[3] Mimeographed Lectures. University of Minnesota. 1929.

well water; namely, soils 1 and 6; and the others have been flooded at some previous time with saline water. A brief description of each profile follows:

Soil 1—Crowley silt loam, cultivated

A 0–5½″ dark mouse gray, brown iron stains around channels of old roots, platy structure, irregular layer of dark, hard, round concretions at 4″ depth, mellow. Tongues or stringers of ashy gray material extend from this horizon to a depth of 20″.

B_1 5½–15″ light gray streaked with brown silt loam, granular structure, compacted.

B_2 15–23″ purplish brown clay, blocky, columnar, very compacted.

C >23″ gray clay, mottled brown stains.

Soil 2—Crowley silt loam, virgin

A 0–6″ dark gray, mellow, fine granular structure, no compaction. Ashy material much less than in soil 1.

B 6–24″brownish gray silt loam, mellow, granular, slightly columnar.

C >24″ gray clay mottled brown, small number of concretions.

Soil 3—Calcasieu fine sandy loam, virgin

A 0–8″ yellowish brown, friable, slightly platy.

B 8–17″ yellowish gray, very fine sandy loam, friable, brown concretions.

C_1 17–27″ light yellowish gray silt loam, brown mottlings, concretions.

C_2 >27″ grayish yellow, bright red mottlings, clay, iron concretions.

Soil 4—Lake Charles fine sandy loam, cultivated

A 0–8″ dark mouse gray, slight brown mottlings, mellow, no compaction.

B 8–20″ light yellow very fine sandy loam, dark brown and black concretions, compacted, beginning columnar development. On slight drying in field has appearance of salt incrustations on surface.

C >20″ light olive gray clay, iron brown mottlings, breaks into blocky lumps.

Soil 5—Silt loam, cultivated

A 0–6″ brownish black, horizontal platy structures, friable.

B 6–27″ light gray, streaked with yellow and red mottlings, silty clay loam. Very sticky and compact, concoidal fracture, development of columns, surfaces of which are dark shiny gray.

C >27″ mouse gray clay, lenses of very fine sand, yellow mottlings, brown and black concretions.

Soil 6—Silt loam, cultivated

A 0–7″ dark brownish gray, friable.

B 7–26″ dark gray silty clay loam, mottled with red and yellow, below 12″ from surface has ashy gray material occurring in tongues, pockets and coating soil particles. Where present in large amounts imparts mellowness to soil. Remainder is compacted and sticky and breaks into angular blocks and shows columnar development, has dark shiny surface.

C >26″ olive gray clay, mottled, small brown and black concretions.

Soil 7—Lake Charles silty clay, cultivated.

A 0–4″ dark gray, with brown mottlings, sticky.

B 4–14″ grayish black heavy silt loam, tongues of grayish white extending to C. Small round concretions. Blocky structure with slight development of columns, very compacted.

C >14″ yellow, mottled with bluish gray, clay. Lime concretions below 18″ from surface, few iron concretions above.

Soil 8—Lake Charles silt loam, cultivated

A 0–8″ dark grayish black, mellow.

B 8–21″ very dark mouse gray silt loam, granular structure, not compacted in

upper part, some compaction in lower part. Slight brown mottlings. Pockets of ashy material.

C >21″ light gray clay, few lime concretions.

In order to study the effect of the various previous floodings upon the chemical properties of the soil, the base exchange capacity and the concentration of the various bases in the exchange complex have been determined together with the hydrogen-ion concentration, total salt content, and soluble alkali.

For the determination of base exchange capacity normal neutral ammonium acetate solution was used as recommended by Schollenberger and Dreibelbis (14). Ten-gram samples were leached with 250 ml. solution in 10 ml. portions on Gooch crucibles by use of gentle suction. The excess ammonium acetate was washed from the soil with neutral ethyl alcohol (70 per cent). The adsorbed ammonium ion was determined by distillation with magnesium oxide as in the common procedure. In the leachate, aliquots of the leachate were used for determining the replaced bases. Calcium was precipitated as the oxalate, ignited, and weighed as the oxide. Magnesium was precipitated as magnesium ammonium phosphate and also determined gravimetrially. Sodium was precipitated from a separate aliquot and weighed as sodium magnesium uranyl acetate as recommended by Piper (10), and from a separate portion of the leachate potassium was precipitated and weighed as potassium sodium cobalti-nitrite (9, 15). The hydrogen-ion concentration was determined colorimetrically by using the soil itself as a filter in a perforated test tube percolator for obtaining a clear solution. Total salt content and soluble alkali were determined according to the method of the Association of Official Agricultural Chemists.

RESULTS AND DISCUSSION

As has been previously pointed out by Kelly and Brown (8), the substitution of sodium for the divalent bases produces two important effects; namely, first, the granular structure of the clay material becomes broken down with the resultant development of extreme impermeability; and, secondly, sodium carbonate is formed as a result of hydrolysis. Since the soils of the rice district have become extremely impermeable the question arose as to whether the impermeability was due to a substitution of sodium ions for divalent ions in the exchange complex. The results of base exchange studies on these soils show that this substitution has taken place to some extent. In table 2 is given a direct comparison of the base exchange values for a cultivated soil, No. 1, which has been flooded only with deep well water, and a virgin soil. Three distinct differences may be pointed out: the increase of exchangeable sodium in the A and the B horizons, the increase in alkalinity and pH value, and the increase in the total exchange capacity of the flooded soil in comparison to the virgin soil. The increase in the absolute amount of sodium in the complex in the A and B horizons averages approximately 100 per cent; however, the

relative increase is very slight—only 1 per cent and 1.5 per cent in the A and B horizons respectively when expressed on the basis of the per cent of sodium in the exchangeable bases. The increase in alkalinity in the A and B horizons indicates that the sodium may be in sufficient concentration to cause instability of the exchange complex with the resultant hydrolysis and production of small amounts of sodium hydroxide or carbonate (1, 4).

The marked increase in the total exchange capacity of the A and B horizons (table 2) is remarkable, since the organic matter has been reduced by cultivation to about one-half of that originally present, from 2.96 per cent to 1.68 per cent. This increase may be explained in one of two ways; namely, the hydrolysis of the mineral constituents of the soil resulting in the formation of substances which have a greater exchange capacity than that of the original minerals from which they were formed; or a change produced in the complex by the adsorbed sodium ions, changing it from the gel form to the sol form and

TABLE 2

Exchangeable bases in virgin and irrigated Crowley silt loam

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	*m.e.**	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
1-A	10.01	4.20	1.25	0.29	11.55	64	26	7.9	1.8	7.1	0.106	0.002
1-B_1	5.40	2.35	1.40	0.08	12.38	58	25	15	0.9	6.2	0.035	0.000
1-B_2	6.48	4.04	1.54	0.51	20.42	52	32	12	4.5	6.0	0.013	0.000
1-C	8.72	5.35	1.90	0.30	18.10	54	33	12	1.8	6.0	0.018	0.002
2-A	4.53	1.87	0.48	0.11	10.0	65	27	6.9	1.6	6.0	0.025	0.000
2-B	3.62	1.62	0.73	0.15	10.7	59	26	12	2.4	5.8	0.106	0.000
2-C	11.31	5.39	2.37	0.32	19.8	58	28	12	1.7	6.1	0.017	0.002

* Milligram equivalents per 100 gm. of dry soil.

thereby increasing the surface and causing through this the increased exchange capacity. Whether this increase is due directly to the hydrolytic action of water itself or is accelerated by the sodium ions present we are unable to state at present. It is interesting to note that the development of the so-called alkali areas require poor drainage as a primary prerequisite for their formation. This has been explained as being essential for the accumulation of soluble salts, principally sodium; for if the soluble salts are removed the complex becomes labile and an extremely compact, impermeable condition develops. Since this latter condition exists in the rice district of Louisiana, it appears that likewise an increase in total base exchange capacity should occur when alkali soils develop. Burgess has offered a possible explanation for this "build-up" in exchange capacity in the presence of increased alkalinity (2).

In the Coastal Prairie Area numerous dome-shaped mounds are found having an average height of 2 feet and a diameter of 16 to 50 feet or more.

These are characteristic topographic features of this region. In table 3 are presented the results of base exchange studies of a virgin mound, soil 3, and a cultivated mound, soil 4. Sample 4 was taken from a field which had been flooded with saline water in 1930. The results show that the saline treatment has materially increased the exchangeable sodium in the A horizon and increased it slightly in the B horizon. There has also been a slight increase in pH of the flooded soil in comparison with the virgin soil.

It is interesting to note that as early as 1901, Heileman and Mesmer (7) reported crop failures on mounds as being due to harmful salts present in them. They further state "The salts found in these soils [mounds] are such as commonly exist in alkali land. In all cases carbonates or black alkali are absent. . . . Alkali accumulation upon the area surveyed will never, perhaps, become a serious menace to the farmer." At the time their report was written the intimate connection between "white" and "black" alkali was not so perfectly

TABLE 3

Exchangeable bases in virgin and irrigated mounds

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
3-A	3.13	1.37	0.20	0.39	4.7	62	27	3.9	7.6	6.0	0.013	0.000
3-B	1.56	1.26	0.20	0.08	4.28	50	40	6.4	2.6	5.8	0.017	0.000
3-C_1	1.79	1.28	0.37	0.12	4.75	50	36	10.4	3.4	5.7	0.002	0.000
3-C_2	8.32	7.05	0.93	0.39	17.60	50	42	5.5	2.5	5.7	0.141	0.000
4-A	3.22	1.56	0.39	0.13	4.00	61	29.4	7.4	2.2	6.6	0.017	0.000
4-B	5.50	3.10	0.68	0.20	7.05	58	32.6	7.2	2.4	6.6	0.053	0.000
4-C	14.13	6.51	1.07	0.42	15.85	64	29	4.8	2.2	7.2	0.021	0.000

understood, and it is not surprising that they assumed that sodium carbonate would not be a menace. The most important point to consider is that the concentration of salt from irrigating waters was at that early date causing barren spots in rice fields. Through the courtesy of Mr. M. N. Stafford, we had occasion to visit some mounds which were barren of rice plants and which had black crusts or deposits upon their surfaces. An analysis of a representative sample from one of these mounds gave the following results: total salts 0.58 per cent, alkali carbonate 0.21 per cent, and soluble humus 0.22 per cent. This sample was taken within 6 miles of several samples reported by Heileman and Mesmer and shows here field evidence that sodium carbonate is being formed from the sodium salts present in the irrigating water as explained by Cummings and Kelley (4) and by Breazale and McGeorge (1). The water used for irrigating these fields was taken from Serpent Bayou and is not very different from the bayou waters reported in table 1. This emphasizes the importance of even small amounts of sodium in irrigating waters when such waters are used over long periods of time.

The effect of one recent flooding with highly saline water upon base exchange is shown in table 4. Soil 5 was flooded with saline water in 1930 at the time the rice crop was heading. The salt concentration was sufficiently high to kill all of the rice plants. In 1931 the field was fallowed, and in 1932 a poor yield of rice was obtained. Soil 6 has always been irrigated with deep well water and was taken from a field situated about one-fourth mile east of soil 5. Both soils are of recent origin, lying immediately north of the marsh fringing the Gulf Coast and have an elevation of 3 feet above the Gulf. It will be noted that

TABLE 4

Exchangeable bases in soils irrigated with fresh and salt water

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
5-A	6.28	2.91	1.31	0.26	8.75	59	27	12	2.5	6.9	0.074	0.004
5-B	19.76	8.00	4.20	0.56	17.60	61	25	13	1.5	7.3	0.071	0.006
5-C	18.01	8.31	3.06	0.47	17.60	60	28	10	1.5	7.6	0.045	0.013
6-A	9.12	2.72	1.10	0.07	8.60	70	21	8.4	0.5	7.1	0.134	0.002
6-B	13.27	6.55	1.22	0.25	13.40	62	31	5.7	1.2	6.8	0.406	0.000
6-C	23.60	10.33	1.50	0.24	18.70	66	29	4.2	0.7	7.5	0.025	0.009

TABLE 5

Exchangeable bases in soils of Lake Charles series which were irrigated with saline water

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
7-A	15.07	6.06	0.98	0.35	18.0	67	27	4.5	1.5	6.7	0.014	0.002
7-B	21.30	8.80	1.50	0.28	20.2	67	28	4.7	1.3	7.3	0.086	0.002
7-C	77.77	11.63	2.10	0.23	19.7	85	13	2.3	0.2	8.2	0.032	0.013
8-A	6.93	2.53	0.80	0.19	9.05	66	24	7.7	1.8	6.6	0.066	0.001
8-B	15.91	4.98	1.75	0.32	14.30	70	22	7.6	1.4	6.9	0.040	0.002
8-C	52.35	8.24	2.18	0.78	21.52	82	13	3.4	1.2	8.2	0.054	0.011

although there has been only a slight increase in the amount of exchangeable sodium in the A horizon, in the B and the C horizons the increase is very marked. This increased sodium content has materially increased the compactness, stickiness, and impermeability and has also increased the alkalinity of the soil. An increase in the exchange capacity in the B horizon of soil 5 is important as it indicates that sodium plays an important part in this phenomenon.

The study of base exchange upon two soils of the Lake Charles series is reported in table 5. Both these soils are giving poor yields and are highly

puddled and in poor physical condition, in spite of the fact that they are relatively high in organic matter. The amount of replaceable sodium, expressed in milliequivalents, is about the same as that for soil 1, but the per cent of sodium in the exchangeable bases is much less. Although the soils of the Lake Charles series contain more organic matter and more calcium than the soils of the Crowley series, apparently these two materials are only slightly effective in overcoming the effects of sodium upon the state of the soil, for soils 7 and 8 are only slightly more permeable than soil 1 and very much less than soil 2. In accordance with the results of other workers (3), it may be concluded that neither the absolute nor the relative amount of sodium in the exchangeable form can be used alone as an index for determining the physical condition of the soil.

Since the profiles of soils 6 and 7 had distinct pockets and stringers of gray material of ashy consistency, which are characteristic features of these soils, separate samples of this material were collected for further study from these

TABLE 6

Comparison of exchangeable bases of normal B with ashy degraded material

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
7-B	21.30	8.80	1.50	0.28	20.2	67	28	4.7	1.3	7.3	0.086	0.002
7-D	16.72	7.32	1.47	0.29	15.8	65	28	5.7	1.3	7.2	0.246	0.001
6-B	13.27	6.55	1.22	0.25	13.40	62	31	5.7	1.2	6.8	0.406	0.001
6-D	9.07	4.07	0.98	0.12	8.55	64	29	6.9	0.8	6.9	0.251	0.002

profiles. The material collected had present considerable amounts of the compacted, darker colored material associated with it. In table 6 a comparison is made between this material, called D, and the normal B horizon from which it was taken. This degraded ashy material shows a much lower total base exchange capacity than the normal B, although the relative proportions of the various bases are very similar. In connection with the increase in the total exchange capacity which is due to the flooding of these soils, a material with a much lowered exchange capacity is present in the B horizon. Therefore, the values for increase in the B horizon do not represent the maximum increase of the compacted material, since all of the B samples contained varying amounts of the degraded material. It appears that this ashy gray material represents accumulation from both degradation of the complex and hydrolysis of the soil minerals and that there is represented here the change from a solonetz to a solodi or a similar change with the production of siliceous material and the removal of iron and aluminum. However, the change has not as yet progressed sufficiently to affect the fertility of these soils to a great extent.

Unless steps are taken to correct this condition we may expect the farmers on these soils to have increasing difficulty in producing profitable crops.

There are a number of references in the literature to the presence of salts in the irrigating waters used on the rice soils of Louisiana and Texas (5, 7, 11, 12). In all cases only the effect of the salt content upon the immediately growing rice crop is considered. Apparently the tacit assumption is made that the salts will be removed when the levees are opened and the fields drained at harvest time or will be removed by the following floodings with purer water or through leaching when the land is fallowed or in upland crop. In no cases are we aware that the effects of saline water upon the physical or chemical properties of these soils have been discussed or reported in the literature. The data presented here show that the waters used in flooding the Coastal Prairie soils have produced effects upon those properties. The small amounts of soluble alkali found should not be taken as an indication of only small changes in alkalinization, as Robinson (13) has pointed out that the percentage of sodium carbonate is no measure of this change and in the absence of carbon dioxide completely deflocculated soil may be formed without the presence of sodium carbonate. The changes induced by the monovalent cations in the irrigating water are analogous to those produced in other regions where irrigation is practiced.

SUMMARY

A study was made of the exchangeable bases in eight soil profiles of the Coastal Prairie Area of Louisiana. It included the evaluation of replaceable bases, base exchange capacity, H-ion concentration, total soluble salts, and soluble alkali. The soils were selected purposely for studying the effect of irrigating waters upon their chemical properties and changes of their physical state; two of the profiles were taken from virgin fields, two from fields which had been irrigated with deep well water, and the remainder from fields that had been irrigated at some previous time with saline water.

The irrigation of the soil caused an increase in the total exchange capacity and an increase in alkalinity. This may be due to the hydrolytic action of water itself, alone or in combination with monovalent basic ions. It appears that the hydrolytic effect is accentuated by the reducing conditions and lowered carbon dioxide production which follow from flooding and irrigation.

The use of saline irrigating water resulted in the greatest increase in the amount of replaceable sodium in the exchange complex, whereas deep well water caused the smallest increase, but in all cases flooding or irrigation caused an increase in comparison with non-flooded soils. The soluble alkali content was low, and in the case of the non-flooded soils no free alkali was present. In accordance with the work of others, it was found that there is no well-defined relationship between the amount or the proportion of exchangeable sodium and the impermeability of the soil to water. Excessive accumulations of soluble carbonate (black alkali) and other soluble salts account for the fact that some of the mounds in rice fields are bare.

The study of typical profiles has shown degradation extending from the A horizon well into the B horizon; the degraded material appears as a coating and is also concentrated in pockets, tongues, or stringers. This degraded material has resulted from the effect of the replacement of other ions in the exchange complex by sodium and also from the effects of reduction and hydrolysis on the mineral decomposition.

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ANION EXCHANGE: II. LIBERATION OF THE PHOSPHORIC ACID IONS ADSORBED BY SOILS

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In part I of this paper it was established that the adsorption of phosphoric acid ions proceeds on the basis of an equivalent exchange with the exchangeable anions of the soil complex. The adsorbed phosphoric acid ions may reappear in the solution when they come in contact with other anions. The liberation of the PO_4 ions should proceed on the same principle of anion exchange reaction which took place when these ions entered the complex. The hydroxyl ions are the most effective anions in PO_4 replacement. By treating the soils with dilute solutions of acids, the greatest part of the adsorbed PO_4 is liberated in consequence of the destruction of the exchange complex by the acids. Together with the PO_4 ions, the products of the destroyed complex also appear in the solution. The anions, like SO_4 and Cl, are adsorbed by soils in very insignificant amounts (5, 8); they do not possess sufficient energy to replace anions like phosphoric acid, which are more strongly adsorbed. The liberation of the adsorbed PO_4, when the soils are treated with alkaline solutions of a low concentration, is due mainly to anion exchange reaction; the PO_4 is replaced by hydroxyl ions of the solutions.

The work presented herewith was undertaken to study the phenomenon of PO_4 liberation when soils containing phosphoric acid ions in adsorbed condition are brought in contact with $Ca(OH)_2$ and NaOH solutions, and to establish the rôle of the anions and cations of these solutions in the process of PO_4 liberation.

SOILS

The experiments were carried out with red sandy and Esdraelon clay soils. Phosphate ions were introduced into the H-soils by shaking the soils with H_3PO_4 solution of a low concentration, which yields the first form of adsorption for H-soils (part I). The excess of the unadsorbed PO_4 was removed by dialyzing through collodion bags. The difference between the amount of PO_4 in the soils after this treatment and its original amount in the soil gave the amount of adsorbed PO_4. The replacement of the exchangeable hydroxyls of the complex by the PO_4 ions was not complete, on account of the insufficient concentration of the PO_4 ions in the solution.

EXPERIMENTAL

The H-soil samples "saturated" with PO_4 were shaken with various quantities of $Ca(OH)_2$ or NaOH solutions. The soils together with the solutions were then transferred to dishes, evaporated, ground, and passed through a 1 mm. sieve. The prepared air-dry soil samples were transferred to small bottles with distilled water, the volume of water used being corrected for hygroscopic moisture so that the total volume was 50 cc. The soils were shaken for an hour and then left to settle for 4 days. After this period the soil extract was filtered and analyzed. The liberated PO_4 (2), the water-soluble Al_2O_3 (1),

TABLE 1

Effect of the addition of $Ca(OH)_2$ on the liberation of adsorbed PO_4 (a water extract of a H-sandy soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH CALCIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of $Ca(OH)_2$ added to the H-sandy soil sample*	Per cent of Ca introduced in relation to the total base exchange capacity			
			m.e.		
1	0.000	0.0	0.0186	6.3	6.65
2	0.197	25.1	0.0108	3.6	6.75
3	0.393	50.0	0.0063	2.1	7.00
4	0.450	57.3	0.0055	1.9	7.00
5	0.489	62.2	0.0051	1.7	7.00
6	0.540	68.7	0.0063	2.1	7.00
7	0.590	75.0	0.0076	2.6	7.00
8	0.786	100.0	0.0104	3.5	7.05
9	0.807	102.8	0.0112	3.8	7.05
10	0.839	106.6	0.0117	4.0	7.05
11	0.892	113.5	0.0123	4.2	7.05
12	0.999	127.1	0.0144	4.9	7.05
13	1.106	140.7	0.0173	5.8	7.05

* The exchange capacity of the 7.5-gm. sandy soil sample is 0.786 m.e.; the PO_4 adsorbed by the H-soil sample is 0.297 m.e.; the difference, therefore, between total anion exchange capacity and the adsorbed PO_4 ions is 0.489 m.e.

Fe_2O_3 (9), and SiO_2 (4a) were determined colorimetrically. All calculations were made on oven-dry weight.

CATIONIC AND ANIONIC EXCHANGE WHEN A $Ca(OH)_2$ SOLUTION IS ADDED TO THE SOIL

In series 1, to a range of 7.5-gm. samples of H-sandy soil containing PO_4 ions in adsorbed condition increasing amounts of $Ca(OH)_2$ were added. This was done to replace gradually the exchangeable hydrogen by Ca ions within the limits of the base exchange capacity of the complex. In certain experiments

the amount of added $Ca(OH)_2$ in milliequivalents surpassed the base exchange capacity of the complex established at pH 7.0. All the calcium in these experiments was completely adsorbed by the complex. The maximum of completely adsorbed calcium by a 7.5-gm. soil with an exchange capacity of 0.786 m.e. was 1.106 m.e. (table 1).

The completely unsaturated soil samples partly, as well as completely, saturated with calcium or with amounts of calcium surpassing the exchange capacity of the sample were shaken with distilled water. The amounts of PO_4 in the solution and the pH were determined.

In general, one may note that with the beginning of a gradual introduction of $Ca(OH)_2$ into the H-soil, the amount of PO_4 in the solution continuously de-

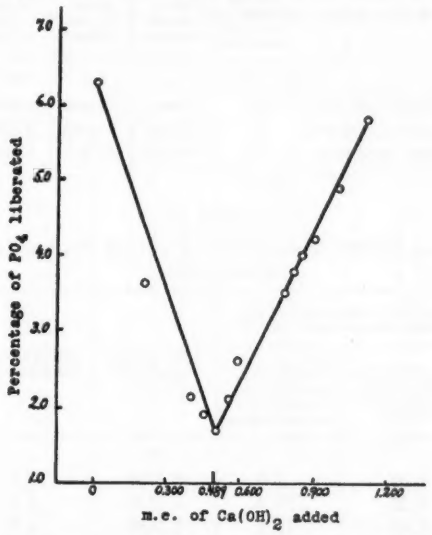

FIG. 1. EFFECT OF THE ADDITION OF $Ca(OH)_2$ ON THE LIBERATION OF PO_4 IN A H-SANDY SOIL

creases until it reaches a certain minimum. By its further introduction the amount of PO_4 begins to increase. This increase continues also when amounts of $Ca(OH)_2$ surpassing the exchange capacity of the soil sample are introduced. The characteristic feature of the curve of PO_4 liberation (fig. 1) is its preliminary descent followed by a sharp bend due to a sudden increase of the PO_4 in the solution. The first gradual decrease of the amount of the water-soluble PO_4 is due to the changes in the physicochemical state of the soil complex, brought about by replacement of its monovalent hydrogen ions with divalent calcium ions. As was found by Gedroiz (3, 4), the degree of dispersibility and of stability of the complex is dependent on the atomic weight and valence of its exchangeable cations. Mattson (6, 7) has established the dependence of the size of charge of the soil colloids, their degree of dispersibility

and swelling, and the dissociation of the adsorbed diffusible ions, on the kind of exchangeable cations. The degree of dispersibility and the dissociation of the adsorbed ions decrease, and the stability of connection between the components of the exchange complex increase when the exchangeable hydrogen is replaced by the divalent calcium. In the case of the less stable H-complex, the PO_4 passes into the solution in higher amounts than in the case of the same

TABLE 2

The degree of stability of the complex and the liberation of PO_4 as influenced by the various exchangeable cations (water extract)

EXPERIMENT NUMBER	MATERIAL FOR EXPERIMENTS	KIND OF CATION INTRODUCED INTO THE COMPLEX	Al IN 50 CC. OF THE EXTRACT	Fe IN 50 CC. OF THE EXTRACT	SiO_2 IN 50 CC. OF THE EXTRACT	PO_4 IN 50 CC. OF THE EXTRACT	pH
			m.e.	*m.e.*	*m.e.*	*m.e.*	
1	7.5 gm. of sandy soil con-	Ca	None	None	0.016	0.014	7.00
2	taining 0.189 m.e. of PO_4	H	0.014	Traces	0.042	0.021	6.65
3	in adsorbed condition	Na	0.014	0.005	0.038	0.076	7.25

TABLE 3

Effect of the addition of $Ca(OH)_2$ on the liberation of adsorbed PO_4 ions (a water extract of a H-sandy soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH CALCIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of $Ca(OH)_2$ added to the H-sandy soil sample*	Per cent of Ca introduced in relation to the total base exchange capacity			
			m.e.		
1	0.00	0.0	0.0205	10.9	6.65
2	0.20	25.4	0.0130	6.9	6.75
3	0.60	76.3	0.0093	4.9	7.00
4	0.65	82.7	0.0143	7.6	7.00
5	0.786	100.0	0.0186	9.9	7.05
6	1.106	140.7	0.0215	11.4	7.05

* The exchange capacity of the 7.5-gm. sandy soil sample is 0.786 m.e.; the PO_4 adsorbed by the H-soil sample is 0.189 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 0.597 m.e.

complex saturated with calcium. The partial destruction of the H-complex causes a liberation of the PO_4 which was connected with it (table 2).

The limit of the decrease of the water-soluble PO_4 is attained when the amount of OH ions of the Ca $(OH)_2$ equals the amount of OH ions left in the complex after the PO_4 ions were introduced. The amount of the non-replaced exchangeable OH ions, calculated according to the difference between the total anion exchange capacity of the complex and the amount of adsorbed PO_4 ions,

equals 0.489 m.e. The action of the $Ca(OH)_2$ introduced in limits of 0.489 m.e. on the PO_4 liberation is entirely different from the action of that introduced beyond this limit. By its introduction into the soil within the limits indicated, only a cation exchange reaction proceeds between the Ca ions of the solution and the H ions of the complex which are in equilibrium with the OH ions. In connection with this cation exchange reaction those changes occur in the physicochemical properties of the complex which are responsible for the decrease of the liberated PO_4. With the introduction of $Ca^{++} \rightleftarrows 2OH^-$

TABLE 4

Effect of the addition of $Ca(OH)_2$ on the liberation of adsorbed PO_4 ions (a water extract of a H-clay soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH CALCIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of $Ca(OH)_2$ added to the H-soil sample*	Per cent of Ca introduced in relation to the total base exchange capacity			
			m.e.		
1	0.000	0.0	0.0581	15.1	6.10
2	0.310	20.0	0.0465	12.1	6.50
3	0.619	40.0	0.0370	9.6	6.70
4	0.929	60.0	0.0317	8.3	6.75
5	1.120	72.4	0.0245	6.4	6.80
6	1.163	75.1	0.0237	6.2	6.85
7	1.238	80.0	0.0306	7.9	6.85
8	1.548	100.0	0.0401	10.4	7.05
9	1.648	106.5	0.0433	11.3	7.05
10	1.698	109.7	0.0465	12.1	7.05
11	1.798	116.2	0.0528	13.7	7.05
12	1.948	>116.2	0.0517	13.4	7.10
13	2.098	>116.2	0.0422	11.0	7.20
14	2.248	>116.2	0.0306	7.9	7.25
15	2.398	>116.2	0.0125	3.2	7.30

* The exchange capacity of the 3.0-gm. clay soil sample is 1.548 m.e.; the PO_4 adsorbed by the H-soil sample is 0.385 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 1.163 m.e.

ions into the H-soil in amounts surpassing the amount of the $OH^- \rightleftarrows H^+$ ions of the complex, an exchange reaction between the OH ions of the $Ca(OH)_2$ and the adsorbed PO_4 ions begins. This anion exchange proceeds simultaneously with the continuing cation adsorption.

In series 2 (table 3) the original soil material for the experiments is the same as in series 1 except that the amount of adsorbed PO_4 per 7.5-gm. sample is 0.189 m.e. The course of PO_4 liberation, as increasing amounts of $Ca(OH)_2$ are added, is entirely similar to that presented in the previous series of experiments.

The decrease of PO_4 in the solution occurs here, too, when $Ca(OH)_2$ is added in amounts which do not surpass in milliequivalents the amounts of the $OH^- \rightleftarrows H^+$ ions of the complex. When the amount of OH ions of the introduced $Ca(OH)_2$ surpasses in insignificant quantities the amount of OH ions of the complex, a sudden increase of PO_4 in the solution takes place.

In series 3 (table 4) a H-clay soil was used. With the addition of increasing amounts of $Ca(OH)_2$ to the H-soil sample, the amount of water-soluble PO_4 gradually decreases until it reaches its minimum, when 1.163 m.e. of $Ca(OH)_2$ is added. An insignificant addition of $Ca(OH)_2$ to the soil above this amount

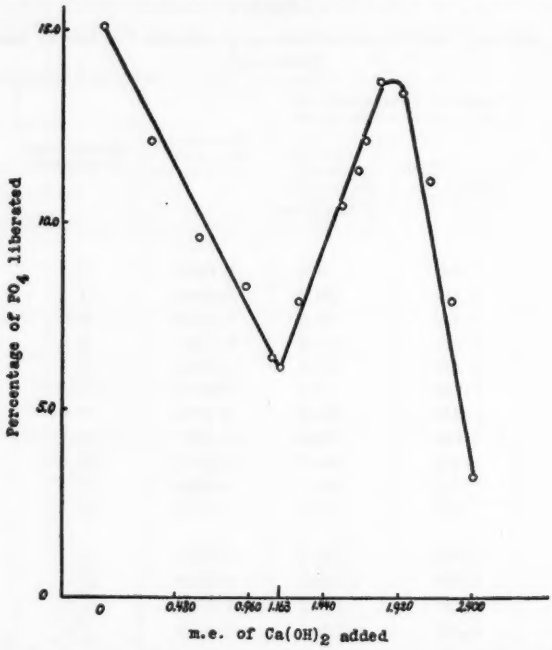

FIG. 2. EFFECT OF THE ADDITION OF $Ca(OH)_2$ ON THE LIBERATION OF PO_4 IN A H-CLAY SOIL

soon gives an increase of PO_4 in the solution. The curve of figure 2 begins to rise with the beginning of anion exchange. Here, too, as in the previous two series of experiments, this point is reached when the quantities of OH ions introduced by the $Ca(OH)_2$ solution exceed in an insignificant measure the amount of OH ions of the complex. The second bending of the curve, which represents the decrease in the amount of water-soluble PO_4, is due to the conversion of the liberated PO_4 into insoluble compounds as a result of introducing into the soil amounts of $Ca(OH)_2$ which cannot be completely adsorbed by it. The maximum amount of $Ca(OH)_2$ which is completely adsorbed by the sample of the clay soil is close to 1.95 m.e. Above this limit some $Ca(OH)_2$ is left in the solution as not adsorbed.

The adsorption of $Ca(OH)_2$ by a H-soil containing PO_4 ions in the exchange complex, in addition to its hydroxyls, proceeds in two phases. In the first place the Ca ions replace only the H ions of the complex which are in equilibrium with the hydroxyls; hence only a cationic exchange takes place. After replacement of all the exchangeable hydrogen ions which were in equilibrium with the OH ions and simultaneously with the continued adsorption of the cations, the anion exchange also begins. The OH ions of the $Ca(OH)_2$ begin to replace the adsorbed PO_4 ions. The phenomenon of replacement, in turn, of the exchangeable hydrogen can be explained by admitting a difference in the degree of dissociation of the $OH^- \rightleftarrows H^+$ ions and of the $PO_4^{\equiv} \rightleftarrows 3H^+$ ions of the complex. The degree of dissociation is probably higher in the first case, where the exchangeable anion is monovalent, than in the second case, where it is trivalent. The phenomenon of H replacement, in turn, can be explained also by the difference in degree of complexity of the exchange reaction, which is less complicated when it is only cationic, and more complicated when it is both anionic and cationic.

The replacement of the adsorbed PO_4 ions continues when amounts of $Ca(OH)_2$ which surpass the total base exchange capacity of the complex are added to the soil. This indicates that the complete exchange reaction between the adsorbed PO_4 ions and the introduced OH ions of the $Ca(OH)_2$ solution is not terminated, even after hydroxyls are added in sufficient quantities to produce a complete exchange of all the adsorbed PO_4 ions. It should be admitted that, in consequence of the more difficult exchange reaction between $PO_4^{\equiv} \rightleftarrows 3H^+$ ions of the complex and the $Ca^{++} + 2OH^-$ ions of the solution, simultaneously with the replacement of the PO_4 ions a part of the introduced $Ca(OH)_2$, without taking part in the exchange reaction, is adsorbed by the complex beyond its exchange capacity, established at pH 7.0.

The low amount of replaced PO_4 in the solution may be due to the secondary reactions which occur between the liberated PO_4 and the Ca(H)- complex, or between the PO_4 and the continuously introduced $Ca(OH)_2$.

The liberated PO_4 which appears in the solution in the form of H_3PO_4 and $Ca(H_2PO_4)_2$ is readsorbed according to the first form for Ca-soils. The readsorption of $Ca(H_2PO_4)_2$ should bring about the appearance of $Ca(OH)_2$ in the solution, which is probably being partly adsorbed by the complex and partly combined with the liberated PO_4, giving with it insoluble compounds.

CATIONIC AND ANIONIC EXCHANGE WHEN A NaOH SOLUTION IS ADDED TO THE H-SOILS

Series 4 and 5 (tables 5 and 6) indicate what influence may be exerted on the liberation of PO_4 by a partial or complete replacement of the exchangeable hydrogen by Na ions. The action of NaOH on the PO_4 liberation also is observed, when it is introduced in quantities which surpass the exchange capacity of the complex.

A different picture of PO_4 liberation is presented, in comparison with the

TABLE 5

Effect of the addition of NaOH on the liberation of adsorbed PO_4 ions (a water extract of a H-sandy soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH SODIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of NaOH added to the H-sandy soil sample*	Per cent of Na introduced in relation to the total base exchange capacity			
			m.e.		
1	0.000	0.0	0.0190	6.40	6.65
2	0.197	25.1	0.0575	19.4	6.80
3	0.393	50.0	0.0575	19.4	7.0
4	0.450	57.3	0.0575	19.4	>7.0
5	0.489	62.2	0.0575	19.4	>7.0
6	0.540	68.7	0.0760	25.7	>7.0
7	0.786	100.0	0.0913	30.8	>7.0
8	0.865	>100.0	0.0997	33.6	>8.6

* The exchange capacity of the 7.5-gm. sandy soil sample is 0.786 m.e.; the PO_4 adsorbed by the H-soil sample is 0.297 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 0.489 m.e.

TABLE 6

Effect of the addition of NaOH on the liberation of adsorbed PO_4 ions (a water extract of a H-clay soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH SODIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of NaOH added to the H-soil sample*	Per cent of Na introduced in relation to the total base exchange capacity			
			m.e.		
1	0.000	0.0	0.0581	15.1	6.10
2	0.310	20.0	0.0972	25.3	6.70
3	0.619	40.0	0.0972	25.3	6.90
4	0.929	60.0	0.0972	25.3	>7.0
5	1.120	72.4	0.0972	25.3	>7.0
6	1.163	75.1	0.0972	25.3	>7.0
7	1.238	80.0	0.1225	31.9	>7.0
8	1.548	100.0	0.1690	42.9	>7.0
9	1.703	>100.0	0.1817	47.2	>8.6

* The base exchange capacity of the 3.0-gm. clay soil sample is 1.548 m.e.; the PO_4 adsorbed by the H-soil sample is 0.385 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 1.163 m.e.

ones obtained, when the exchangeable hydrogen is replaced by Ca ions (figs. 3 and 4). As a certain amount of sodium is introduced into the H-complex the PO_4 in the solution increases at once. The amounts of liberated PO_4,

0.0575 m.e. for the sandy soil, and 0.0972 m.e. for the clay soil, are kept on a constant level until the OH ions of the NaOH are introduced in quantities which do not exceed those of the exchangeable hydroxyls left unreplaced by the PO_4 ions. When the OH ions are introduced into the soil in quantities

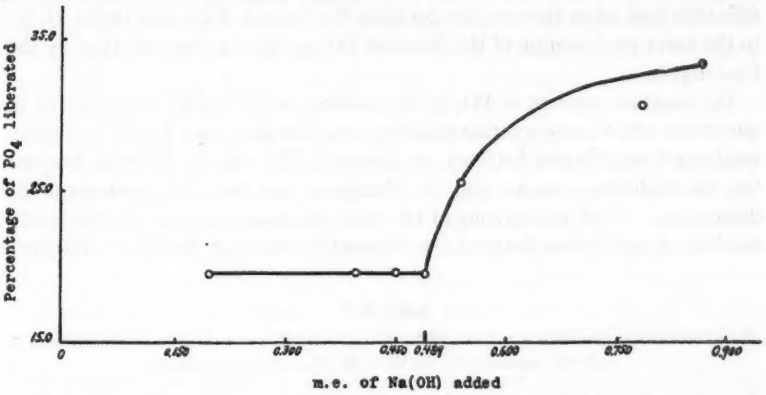

FIG. 3. EFFECT OF THE ADDITION OF NaOH ON THE LIBERATION OF PO_4 IN A H-SANDY SOIL

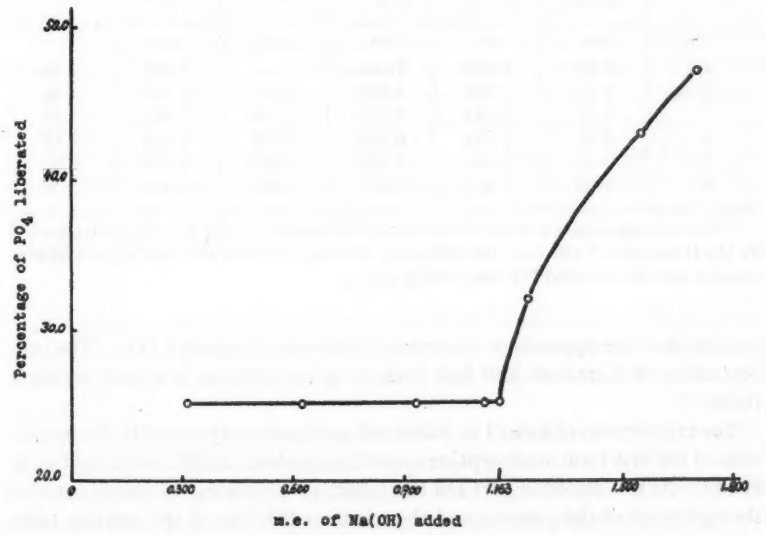

FIG. 4. EFFECT OF THE ADDITION OF NaOH ON THE LIBERATION OF PO_4 IN A H-CLAY SOIL

which surpass these limits only slightly, the amount of liberated PO_4 increases suddenly, as a result of the beginning of the anion exchange reaction, and this increase continues gradually with the further introduction of NaOH. Simultaneously with the anion exchange a continued cation exchange proceeds.

The presence of higher amounts of PO_4 in the solution as a result of the addition of NaOH, as compared with the amounts of PO_4 when similar quantities of $Ca(OH)_2$ are added, may be due: (*a*) to the increased dispersibility of the complex, its easier destruction, and the higher degree of dissociation of the diffusible ions when the complex contains Na instead of Ca ions (table 2); (*b*) to the lower readsorption of the liberated PO_4 by the Na-complex than by the Ca-complex.

The constant amount of PO_4 in the solution, when NaOH is introduced in quantities which cause a cation exchange reaction only, may be due to a finely established equilibrium between the liberated PO_4 and its different fixators, like the exchange complex and the aluminum and iron, the products of its destruction. With the starting of the anion exchange reaction the previously established equilibrium between the different fixators and the PO_4 is destroyed

TABLE 7

The partial destruction of the complex and the liberation of PO_4 as influenced by the addition of different quantities of NaOH to the H-soils (water extract)

EXPERIMENT NUMBER	NaOH ADDED TO THE H-SANDY SOIL SAMPLE*	Al IN 50 CC. OF THE EXTRACT	Fe IN 50 CC. OF THE EXTRACT	SiO_2 IN 50 CC. OF THE EXTRACT	PO_4 IN 50 CC. OF THE EXTRACT	pH
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
1	0.25	0.014	Traces	.....	0.047	7.00
2	0.33	0.014	0.005	0.040	0.045	7.00
3	0.40	0.014	0.005	0.039	0.047	7.05
4	0.50	0.014	0.006	0.037	0.047	7.05
5	0.66	0.014	0.005	0.038	0.076	7.25
6	1.00	0.014	0.011	0.041	0.116	7.50

* The exchange capacity of the 7.5-gm. sandy soil sample is 0.786 m.e.; the PO_4 adsorbed by the H-sample is 0.189 m.e.; the difference, therefore, between the total anion exchange capacitv and the adsorbed PO_4 ions is 0.597 m.e.

as a result of the appearance of increased amounts of replaced PO_4. The concentration of aluminum and iron present in the solution is almost constant (table 7).

The experiments of series 1 to 5 afforded an opportunity to verify the mechanism of the first form of adsorption according to which the PO_4 was fixed by the H-soil. As was stated in part I of this paper, an equivalent exchange between the hydroxyls of the complex and the trivalent PO_4 ions of the solution takes place in this form of adsorption. The correctness of this statement is confirmed by the results of the experiments in the present work, for the amount of exchangeable hydroxyls left unreplaced together with the amount of adsorbed phosphoric acid compose in milliequivalents exactly the total anion exchange capacity of the complex; that is, the adsorption of PO_4 proceeded on the principle of an equivalent exchange between the trivalent phosphoric acid ions and the hydroxyls of the soil complex.

EFFECT OF LIMING AND INTRODUCTION OF PHYSIOLOGICALLY ALKALINE SALTS INTO THE SOIL UPON THE LIBERATION OF ADSORBED PO_4

This study throws some light on the contradictory results obtained by different investigators regarding the liming of acid soils for the purpose of transforming the adsorbed PO_4 into an available form. The apparently contradictory phenomena in the process of PO_4 liberation which are observed when various acid soils are limed, take place also, as is shown in this work, when various quantities of $Ca(OH)_2$ are introduced into the very same unsaturated soil containing a definite amount of adsorbed PO_4.

The liming may have a favorable influence on the liberation of the adsorbed PO_4 when the exchangeable hydrogen ions which are in equilibrium with the hydroxyls are completely replaced, and when an excessive amount of $Ca(OH)_2$ is added. This excessive $Ca(OH)_2$ is needed for the replacement of the adsorbed PO_4. Part of the replaced PO_4 remains in the solution and part is readsorbed by the Ca-complex. The newly formed combination of PO_4 and Ca-complex, as will be seen in a later paper, is very unstable. As a result of hydrolysis of the exchangeable calcium which is in combination simultaneously with the adsorbed H_2PO_4 ion and with the exchange complex, or when this calcium is attacked by very weak acids, the aforementioned combination is broken up, causing the appearance of PO_4 in the solution.

The appearance of larger amounts of water-soluble PO_4 in the soil solution when physiologically alkaline fertilizers are introduced is the result of the action of the residual alkalinity on the exchange complex containing PO_4 in adsorbed condition. The basic ion, entering the complex, causes certain changes in the physicochemical state of the latter which favor the liberation of the PO_4. The adsorbed PO_4 may also be liberated by exchange with hydroxyls of the alkaline salts which may appear in the solution as a result of the introduction of physiologically alkaline fertilizers.

SUMMARY

The course of phosphoric acid liberation when $Ca(OH)_2$ or NaOH solutions are added to H-soils containing PO_4 ions in adsorbed condition, was studied. The influence of the exchangeable Ca, Na, and H ions on this liberation was considered.

In preparing the soil material for the study of PO_4 liberation, the trivalent phosphoric acid ions were introduced into the H-soils.

The exchange reactions, which begin as $Ca(OH)_2$ or NaOH solutions are added to the soil, proceed in two phases. In the first phase only a cationic exchange takes place between the Ca or the Na ions of the introduced solutions and the exchangeable H ions which are in equilibrium with the hydroxyl ions. As the replacement of these H ions is complete, the second phase of the exchange reactions proceeds. This exchange is anionic as well as cationic. It proceeds between the OH ions of the $Ca(OH)_2$ or NaOH solutions and the adsorbed PO_4 ions and, simultaneously, between the Ca or Na ions of the solutions and the exchangeable hydrogen ions which are in equilibrium with the adsorbed PO_4 ions.

The distribution of the reaction of hydrogen replacement into two phases can be explained by the difference in the degree of dissociation of the $OH^- \rightleftarrows H^+$ ions and of the $PO_4''' \rightleftarrows 3H^+$ ions of the complex and the difference in the degree of complexity of the exchange reaction, which is in one case only cationic and in the other both anionic and cationic.

A gradual decrease in the amount of water-soluble PO_4 as the exchangeable hydrogen which is in equilibrium with the OH ions is gradually replaced by Ca ions, is directly related to the changes in the physicochemical state of the complex. The increase of PO_4 in the solution when additional amounts of $Ca(OH)_2$ are applied to the soil occurs with the beginning of PO_4 replacement. This anion exchange reaction takes place only when the quantity of OH ions introduced exceeds the quantity of OH ions which are present in the complex. The introduction of $Ca(OH)_2$ in amounts which can not be completely adsorbed by the soil causes a transformation of the liberated PO_4 into an insoluble condition.

The amount of PO_4 liberated is kept on an equal level as long as the introduced Na replaces only the exchangeable hydrogen ions which are in equilibrium with the OH ions. When NaOH is added in amounts of milliequivalents exceeding the amount of exchangeable OH ions of the complex, an anion exchange reaction begins between the additionally introduced OH ions and the adsorbed PO_4 ions.

The difference in the amount of liberated PO_4, when similar amounts of Ca or Na are introduced into the complex, is due to the differences in the degree of dispersion and stability of the calcium and sodium complexes and to the degree of dissociation of their diffusible ions.

The amount of PO_4 recovered in the solution, after all exchange reactions have taken place, appears to be the result of a final established equilibrium between the liberated PO_4, on one side, and the exchange complex, the products of its destruction, and the electrolytes of the solution, on the other.

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SORPTION OF LIQUIDS BY SOIL COLLOIDS: I. LIQUID INTAKE AND SWELLING BY SOIL COLLOIDAL MATERIALS

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The present work was undertaken with the view of determining the factors governing the chemical melioration and stabilization of soils for agricultural and road building purposes. The experimental part of the study was designed with the following objectives in mind: (*a*) the development of a simple and accurate technic suitable for making routine analyses of the sorption of liquids by soils and soil colloids; (*b*) the formulating of a clearer conception of the physico-chemical properties of the colloidal clay particle in order to be able to predict with a higher degree of certainty the behavior of the soil under conditions of highway construction and agricultural manipulation; and (*c*) the obtaining of data which would be of value in critically examining the existing theories as to the mechanism of the swelling of soils and other colloidal systems.[3]

EXPERIMENTAL PRINCIPLES

When powdered soil colloids are placed in contact with a free water surface, water is taken up or sorbed. Although the exact nature of water sorption is not completely understood, the original assumption was made in this study that part of the water is taken up to fill the macro- and micro-pores and that the remaining sorbed amounts are used to produce the phenomenon of swelling. Since certain non-polar liquids such as benzene do not cause significant swelling when sorbed by soil colloids, they can be used to measure the pore space of the system. On the basis of these assumptions the amount of swelling water would be the difference between the sorbed amounts of water and benzene. Although it is realized that benzene may produce a small amount of swelling, that the size of the benzene molecule may prevent its entering all the pores that would sorb water, and that the total pore space in the presence of water

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[2] Joint contribution from the Missouri State Highway Department and the University of Missouri, department of soils. Missouri Agricultural Experiment Station, Journal Series Paper No. 368.

[3] The data obtained will be analyzed in Part II from the point of view of (*a*) the thermodynamic treatment of Katz; (*b*) the Donnan membrane equilibrium as developed by Wilson, Procter, and Wilson and by Mattson; (*c*) the mechanistic, hydrodynamic treatment of Terzaghi; and (*d*) the concept of hydration and molecular orientation at surfaces and interfaces as instigated by the work of Hardy, Harkins, and Langmuir.

may be restricted somewhat by the swelling process, this method of measuring swelling offers an opportunity of obtaining valuable data concerning the behavior of soil colloids under conditions of water sorption.

The colloids, following their extraction, were electrodialyzed to form H-saturated systems thereby eliminating the variable factor of the nature of the adsorbed cation. From these H-systems, other cations were substituted on the surface of the colloid by adding the respective hydroxides. They were air-dried and ground to pass a 300-mesh screen in order to minimize the effect of particle size. They were then dried in a desiccator over P_2O_5. This method of drying was chosen in order to avoid any irreversible changes as a result of heating the colloid. The moisture content was reduced almost to the same value as in oven drying.

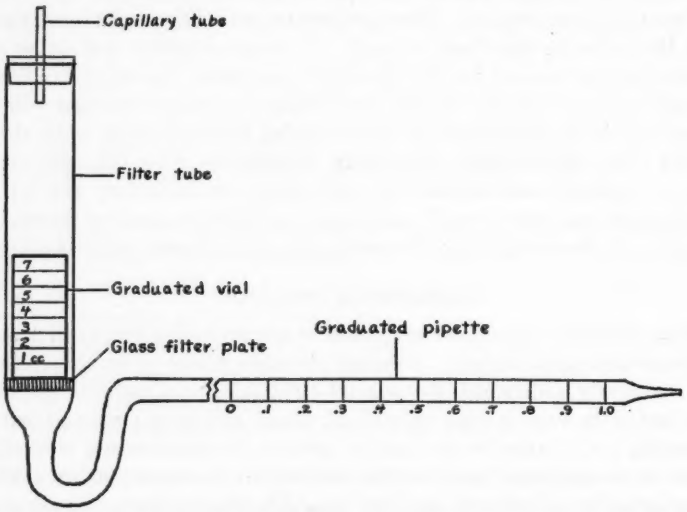

FIG. 1. APPARATUS FOR MEASURING THE LIQUID SORPTION AND SWELLING OF SOIL COLLOIDS

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used in this study was constructed upon the principle of measuring the intake of liquid by powdered colloids through a porous plate and avoiding a positive or negative pressure head of the liquid. It so happened that in its final form it resembled quite closely the Freundlich apparatus (3) which was devised independently about the same time. The apparatus most frequently used (fig. 1) consists of a Jena glass tube with a fused-in sintered-glass filter disc; the Jena tube was connected to a microburette by a small glass tube. The microburette had a capacity of 1 cc. and could be read to 0.002 cc. When the swelling of bentonite was measured, a three-way stopcock connected to a water reservoir was inserted between the Jena glass tube

and the microburette. Such a connection permitted the introduction of more water as sorption progressed. Liquids which dissolve or attack stopcock grease cannot be used with the stopcock connection, however.

A weighed amount of powdered colloid, usually 0.5 gm., was poured into a calibrated glass tube, 1 cm. in diameter and 2 cm. long, closed at the bottom with a fine silk cloth; the colloid was lightly packed with a glass pestle. This tube was placed upon the moist filter disc in the apparatus; the apparatus was then closed with a rubber stopper. A glass capillary through the stopper and another at the end of the burette provided equal pressures at both surfaces of the sorption liquid, and at the same time rendered negligible the loss from evaporation. Measurements were made in an air thermostat maintained at a temperature of 30°C. The liquid intake was determined by reading the burette at different time intervals. Most of the experiments could be terminated after 24 hours, since this time was usually sufficient for the saturation of the system with the liquids in question. Duplicate determinations could be made to check within a deviation of from 2 to 5 per cent. The simplicity and accuracy of the technic render it most adaptable to routine laboratory analyses.

Since the sorption of liquids is intimately related to surface phenomena, the amount of sorption should be expected to vary with the nature of the sorbing surface and the properties of the sorbed liquid. In order to obtain data that would shed some light on these surface reactions experiments were so designed as to employ (*a*) colloids of varied chemical constitution both as to their crystal lattice compositions and as to the nature of the ions adsorbed upon the colloidal surfaces, and (*b*) liquids possessing a wide range in their dielectric properties but maintaining a certain similarity in their molecular structures.

The following colloids, extracted from widely different soils and electrodialyzed, were used in this study:

1. Cecil colloid from the subsoil of a clay loam from Alabama. SiO_2-sesquioxide ratio, 1.3.
2. Susquehanna colloid from the well-oxidized horizon of the Susquehanna clay from Alabama. SiO_2-sesquioxide ratio, 2.3.
3. Putnam colloid from the heavy layer of a silt loam from Missouri. SiO_2-sesquioxide ratio, 3.2.
4. Wabash colloid from an alluvial clay from Missouri. SiO_2-sesquioxide ratio, 3.2.
5. Lufkin colloid from the surface layer of a Black Belt soil from Alabama. SiO_2-sesquioxide ratio, 3.8.
6. Bentonite, a colloidal fraction from commercial Wyoming bentonite. SiO_2-sesquioxide ratio, 5.0.

The different liquids employed were: distilled water; absolute methyl, ethyl, propyl, and amyl alcohols; carbon tetrachloride; benzene; toluene; xylene; aniline; and nitrobenzene. The alcohols were purified by boiling with calcium oxide and subsequent distillation; the other liquids by repeated distillation.

EXPERIMENTAL RESULTS

The size of secondary particles and sorption of liquids. In order to determine what effect the fineness of grinding the dry colloidal material has upon the

sorption of liquids, the Putnam colloid was ground to give three different sizes of particles: (*a*) particles smaller than 0.053 mm. in diameter, (*b*) particles ranging from 0.053 to 0.10 mm., and (*c*) particles ranging from 0.10 to 0.25 mm. The intake of both water and benzene was studied, and the results are shown in table 1. The rate of water sorption during the first few minutes was rather rapid after which it decreased to almost zero at the end of 24 hours. This rapid intake of water during the early stages of the experiment is primarily the result of filling the capillary pores. Benzene sorption was complete after 5 minutes, indicating that all the available capillaries had been filled. When the

TABLE 1

The relationship between water intake and size of the secondary particle of the soil colloid

TIME	WATER INTAKE BY 0.5 GM. OF COLLOID					
	(*a*)*		(*b*)		(*c*)	
minutes	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
1	0.571	0.675	0.615	0.622	0.602	0.583
2	0.656	0.705	0.645	0.645	0.617	0.610
3	0.681	0.715	0.655	0.655	0.625	0.618
4	0.691	0.725	0.660	0.662	0.629	0.623
5	0.701	0.730	0.665	0.667	0.632	0.625
10	0.724	0.750	0.680	0.680	0.645	0.640
20	0.746	0.768	0.691	0.693	0.654	0.650
30	0.761	0.777	0.698	0.700	0.660	0.657
60	0.781	0.792	0.711	0.713	0.672	0.667
120	0.800	0.809	0.726	0.729	0.687	0.680
1,200	0.858	0.864	0.779	0.789	0.750	0.737
1,260	0.859	0.864	0.780	0.791	0.753	0.740
1,380	0.865	0.867	0.784	0.797	0.760	0.746
1,440	0.867	0.868	0.785	0.799	.....	.....
1,660	0.871	0.870	0.789	0.803	0.767	0.754
2,640	0.898	0.893	0.815	0.831	0.802	0.787
2,820	0.901	0.894	0.819	0.836	0.806	0.790

* (*a*) Particles smaller than 0.053 mm.
(*b*) Particles from 0.053 to 0.10 mm.
(*c*) Particles from 0.10 to 0.25 mm.

sorbed amount of benzene is subtracted from the sorbed water to obtain the swelling water it is seen that the swelling of particles with diameters less than 0.10 mm. is practically the same. The particles larger than 0.10 mm. seemingly show the largest swelling. This is probably due to a dispersion effect of the water. On the basis of these data colloids were ground to give particles smaller than 0.1 mm. in cases where only comparative values were desired. In all other experiments they were smaller than 0.05 mm.

The effect of dielectric constant and molecular structure on the sorption of liquids. If swelling is a phenomenon associated with the electrical field forces on the surface of the colloidal particles, it should also be expected to be a function of

the electrical properties of the liquid. Consequently, there should be a correlation between the sorption of a liquid by powdered soil colloids and the dielectric constant of the liquid. The different attempts of other investigators to connect dielectric constants with swelling will be discussed later.

The data obtained in this study are given in tables 2 and 3. Table 2 shows the relationship between the dielectric constant and sorption when more or less non-polar liquids are used. In table 3 the correlation between sorption and

TABLE 2

*The intake of non-polar liquids and dielectric constants**

LIQUID	INTAKE	DIELECTRIC CONSTANT
	cc.	
CCl_4	0.318	2.22
Benzene	0.318	2.26
Toluene	0.323	2.36
Xylene	0.324	2.48
Aniline	0.356	7.00
Nitrobenzene	0.373	34.30

* Particle size <0.1 mm.

TABLE 3

*The sorption of polar liquids and dielectric constant**

LIQUID	INTAKE	DIELECTRIC CONSTANT D	SWELLING S	D/S
	cc.			
H-OH	0.99	76.0	0.58	131
H_3C-OH	0.66	31.9	0.25	128
H_5C_2-OH	0.60	24.1	0.19	127
H_7C_3-OH	0.57	20.5	0.16	128
$H_{11}C_5$-OH	0.53	14.6	0.12	122
Pore space CCl_4	0.41	2.2	....	...

* Particle size <0.053 mm.

swelling and the dielectric constant of water and various alcohols is shown. Both sets of data indicate that a relationship between swelling and the dielectric properties of the liquid exists only if there is a certain similarity in the molecular structure of the liquids. The data in table 3 show that the swelling of colloids in consequence of the sorption of a polar liquid of the water type may be expressed more or less quantitatively by the equation

$$\frac{L - P}{L' - P} = k \frac{D}{D'}$$

Where L = cc. of sorbed liquid with dielectric constant, D.
L' = cc. of sorbed liquid with dielectric constant, D'.
P = cc. of pore space as measured with a non-swelling liquid.
k = constant.

Since the structural similarity of the molecules in different liquids or the similarity of their electric fields is, according to Harkins (4), expressed by their

TABLE 4

Water intake as a function of the SiO_2-sesquioxide ratio

COLLOID	INTAKE	PORE SPACE	SWELLING	SiO_2/R_2O_3	BASE EXCHANGE CAPACITY, M.E. PER 100 GM.
	cc.*	cc.*	cc.*		
H-Cecil	0.655	0.620	0.035	1.3	13
H-Susquehanna	0.830	0.550	0.280	2.3	47
H-Putnam	0.870	0.390	0.480	3.2	65
H-Wabash†	0.920	0.450	0.470	3.2	78
H-Lufkin	0.990	0.410	0.580	3.8	82
H-Bentonite	1.885	0.725	1.160	5.0	95

* Per 0.5 gm. colloid. Sorption of water by all colloids except bentonite was practically complete after 24 hours; bentonite intake required 7 days.

† Relatively high content of organic colloid influences sorption considerably.

TABLE 5

Water intake by Putnam colloid saturated with different cations

CATION	INTAKE*	PORE SPACE	SWELLING
	cc.†	cc.†	cc.†
Li	3.250	0.625	2.625
Na	2.725	0.625	2.100
K	0.733	0.480	0.253
Ba	0.873	0.450	0.423
Ca	0.954	0.500	0.454
H	0.900	0.490	0.410

* The end readings for K-, Ba-, Ca-, and H-colloids were taken after 24 hours, and those for the Li- and Na-colloids after 56 hours. The values for Li- and Na-colloids are somewhat too low as a result of diffusion of the highly dispersed colloid through the filter plate.

† Per 0.5 gm. colloid.

miscibilities, the values for D/S in table 3 should be expected to deviate from that for water with decreasing solubility of the alcohols in water; this is their actual behavior. It may be emphasized that because of the experimental definition of "swelling" as used in this investigation, the aforementioned formula can at present be looked upon only as a semi-quantitative expression of the swelling of soil colloids in liquids with a field structure similar to that of water.

Influence of the nature of the colloidal surface on water sorption. It has been shown by Baver (2), Mattson (6), Freundlich (3), and others that the chemical composition of the colloid (crystal lattice structure determined by the SiO_2-sesquioxide ratio of the colloid) and the nature of the adsorbed ions influence such physicochemical properties as viscosity, plasticity, and volume changes. Freundlich, Mattson, Anderson (1), Woodman and Chapman (7), Joseph and Oakley (5), and others have demonstrated a certain apparent functional correlation between water absorption and the nature of the colloidal particle. These data, however, do not permit a complete discussion of the various factors involved, since the nature of the adsorbed ions and their effects on water sorption were not extensively studied. Inasmuch as various colloids with different crystal lattices and saturated with various ions were studied somewhat in detail in this investigation with regard to water sorption and swelling, considerable data have been accumulated which promise to shed some light on the nature of the swelling process. A complete discussion of the data obtained will be reserved for Part II of this study; it will suffice at this time to mention briefly a few of the typical results obtained. The data in table 4 show that water sorption and swelling increase with the SiO_2-sesquioxide ratio of the colloid, indicating that sorption is correlated with the constitution of the alumino-silicate responsible for the properties of the colloid. The data in table 5 indicate vividly that the nature of the adsorbed ion plays a distinct part in the phenomenon of water sorption. It is especially striking that the H-, Ba-, and Ca-ions should be similar in their behavior and that the K-ion should have such a repressing effect upon the water intake of these colloidal systems. These relationships are specific for colloids other than the Putnam colloid. Their theoretical and practical significance will be discussed later.

SUMMARY

A simple method for measuring the liquid intake and the swelling of soils and soil colloids is described.

The sorption of various liquids by powdered soil colloids was measured. It was found that swelling, defined as the difference between sorption of swelling liquid and intake of non-swelling liquid, is a function of form and intensity of the electric field around the liquid molecules. The swelling of soil colloids in liquids having a water-like structure, as related to the dielectric constant, is expressed by a simple formula.

The influence of the SiO_2-sesquioxide ratio and the nature of the adsorbed cation was studied.

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THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XIV. THE ELECTROKINETICS OF HYDROUS OXIDES AND THEIR IONIC EXCHANGE[1]

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When a solution of a metallic salt such as the chlorides of tin, ferric iron, and aluminum is treated with alkali there is formed a voluminous gelatinous precipitate called "hydroxide," to which a definite formula $X \cdot OH_y$ is usually assigned. These compounds have long been known to be colloidal in nature, and usually the hydrous oxides formed by treating with water or dilute alkali carry a positive charge. It was very early recognized that the hydroxides thus formed carry some of the anion in a form that is difficult to remove by dialysis through a semi-permeable membrane, although many attempts have been made to obtain a "pure colloid."

Under the ordinary conditions of preparation, that is by dialysis of an easily hydrolyzed salt such as the acetate, nitrates, or chlorides, the sols of a series of hydroxides, such as aluminum, ferric, zinc, and copper hydroxides, are always positively charged. Powis (4), however, working with the preparation of colloidal ferric hydroxide, showed that the sign of the charge is a matter of ionic environment during the preparation. Colloidal ferric hydroxide prepared by dialysis of the chloride is positively charged, which is attributed by Powis to a preferential adsorption of the ferric ion, which is present in excess. This ion is preferentially adsorbed by the colloid particle, and confers its positive charge on the colloidal micells. By allowing a dilute solution of ferric chloride to run slowly to a slight excess of dilute alkali hydroxide, Powis succeeded in preparing a negatively charged ferric hydroxide. The negative charge of the resulting sol in this case is attributed to a preferential adsorption of the hydroxyl ion from the alkaline solution.

Mattson (1) in a series of investigations has shown that the charge of a large number of colloidal materials is a function of the pH in the dispersion medium

[1] Editor's Note: It will be noted that this paper bears the same serial number (XIV) as the paper by A. J. Pugh published in the May 1934 issue of SOIL SCIENCE (vol. 37, no. 5, p. 403). The paper by Pugh and a subsequent one entitled "Laws of Soil Colloidal Behavior: XV. Ionic Exchange with Hydroxides," which appeared in the August 1934 issue of SOIL SCIENCE (vol. 38, no. 2, p. 161), are not part of Mattson's series and should be numbered papers I and II of Pugh's series "Laws of Soil Colloidal Behavior."

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and of the nature of the anions in combination. The colloids investigated included a great many different materials, such as the hydroxides of iron and aluminum, phosphates, silicates, humates, and the colloidal material that is present in the soil. All of these precipitates fall into a large class of substances, and may be defined as colloidal ampholytes, the main factor governing the sign of the charge being the pH of the external medium. In order to understand the processes as it affects other hydroxides the work has been extended in this paper to include the hydroxides of other metals, which can be isoelectrically precipitated.

EXPERIMENTAL METHOD

The method employed for preparing the compound for a determination of the isoelectric point, is the same as has previously been employed by one of us. Measured portions of a dilute solution of the salt of the metal were placed in a

TABLE 120

The $Yt(NO_3)_3$ + NaOH system

A. 10 m.e. $Yt(NO_3)_3$ in 1,000 cc.
B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	1.4	Clear	Clear	.....	7.9
20	1.5	Clear	Clear	.....	....
20	1.6	Rapid	xxxx	Slow +	8.9
20	1.7	Rapid	xxxx	Slow −	9.0
20	1.8	Rapid	xxxx	−0.7	9.2
20	1.9	Rapid	xxxx	−1.2	9.5
20	2.3	Rapid	xxxx	−2.0	10.7
20	3.0	Rapid	xxxx	−2.7	11.0

Plus water to make total volume 50 cc. Isoelectric pH 8.95.

beaker, and the pH range at which maximum flocculation occurred was obtained by a preliminary titration with sodium hydroxide. A series of precipitates were then prepared to cover this range, the pH being adjusted at short intervals by NaOH in progressively increasing quantities, the total volume in each case being made up to 50 cc. The flocculation after mixing, and after standing overnight is recorded in the tables, x representing slight flocculation, xx about half complete, xxx nearly complete, and xxxx complete flocculation. The flocs were allowed to stand overnight, the pH of the supernatant liquid and the cataphoresis measurements were made in the manner previously described.

THE ISOELECTRIC POINT

In previous publications by Mattson and Parberry and by Mattson the isoelectric precipitation of aluminum and ferric hydroxides (1, III), stannous

hydroxide, and antimony oxychloride (3) has been discussed. In this work we have studied the precipitation of hydroxides by NaOH from the following salts: $Yt(NO_3)_3$, $LaCl_3$, $TiCl_4$, $Zr(NO_3)_4$, $CeCl_4$, $Th(NO_3)_4$, $SnCl_4$, $Pb(NO_3)_2$, $ZnCl_2$, $MgCl_2$, $CoCl_2$, and $NiCl_2$.[3] The results are shown in tables 120–130.

The precipitates flocculate rapidly at the isoelectric point as well as over a certain range on either side of this point. Beyond this zone of rapid flocculation more or less stable sols are usually formed, especially in dilute solutions.

TABLE 121

The $LaCl_3$ + NaOH system

A. 10 m.e. $LaCl_3$ in 1,000 cc.
B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	1.5	Clear	Clear	.....	8.2
20	1.7	Clear	Clear	.....	8.2
20	1.8	Clear	xxxx	+1.5	9.2
20	1.9	Clear	xxxx	+0.9	10.3
20	2.0	Rapid	xxxx	±0.0	10.4
20	2.3	Rapid	xxxx	−0.7	10.9
20	2.9	Rapid	xxxx	−1.5	11.1
20	3.2	Rapid	xxxx	−2.0	11.5
20	3.5	Rapid	xxxx	−v. slow	11.6

Plus water to make total volume 50 cc. Isoelectric pH 10.4.

By direct observation or by interpolation we find the following order for the isoelectric pH as far as investigated:

Isoelectric pH of various hydroxides

	HYDROXIDE												
	Sn(ic)	Ti(ic)	Sb	Sn(ous)	Zr	Ce	Th	Fe(ic)	Al	Yt	Zn	La	Pb
Isoelectric pH.....	3.9	4.8	5.6	6.6	6.7	6.75	6.85	7.1	8.1	8.95	10.3	10.4	11.0

Two hydroxides, Mg and Ni, remained electropositive up to pH 12.0, whereas Co appeared to be practically isoelectric at pH 11.4. Although no high degree of accuracy can be claimed for these values, since it is extremely difficult to measure the movements of gelatinous flocs, it is evident that there exists a general relationship between the isoelectric point of the hydroxides and the

[3] In the absence of non-polarizable electrodes it is not possible to determine the charge of the precipitates at pH values above 12.0 or below 3.0, because of the evolution of gas at the electrodes, which causes a displacement of the liquid within the cell.

position the metals occupy in the periodic system. Thus the isoelectric pH increases with the metallic and electropositive character as we pass from a lower to a higher atomic weight within a group of elements. The trivalent elements, Al, Yt, and La, give isoelectric hydroxides at pH 8.1, 8.95, and 10.4

TABLE 122

The $TiCl_4$ + NaOH system

A. 10 m.e. $TiCl_4$ in 1,000 cc.
B. 50 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	7.0	Opal	xx	+3.0	3.6
20	7.8	Opal	xxx	+3.0	4.0
20	8.0	Slow	xxxx	+3.0	4.1
20	8.2	Rapid	xxxx	+1.2	4.6
20	8.4	Instant	xxxx	+0.6	4.6
20	8.5	Instant	xxxx	−1.2	5.0
20	8.6	Rapid	xxxx	−2.7	6.4
20	8.8	Slow	xxx	−3.0	6.7
20	9.0	Opal	xxx	−3.0	7.4

Plus water to make total volume 50 cc. Isoelectric pH 4.8.

TABLE 123

The $Zr(NO_3)_4$ + NaOH system

A. 10 m.e. $Zr(NO_3)_4$ in 1,000 cc.
B. 10 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	8.0	Clear	Clear	.....	5.4
20	9.0	Instant	xxxx	+3.0	6.2
20	9.5	Instant	xxxx	+3.0	6.5
20	9.75	Instant	xxxx	+2.5	6.5
20	10.0	Instant	xxxx	+1.7	6.5
20	10.25	Clear	xx	−2.7	7.0
20	10.5	Clear	x	.....	7.1
20	11.0	Clear	Clear	.....	8.6

Plus water to make total volume 50 cc. Isoelectric pH 6.7.

respectively. The same applies to the tetravalent elements in the fourth group, Ti, Zr, Ce, and Th, although the difference between the latter three is very small. Cerium, which in the normal form is trivalent, was oxidized to the tetravalent form by the addition of a few drops of hydrogen peroxide before precipitation.

The isoelectric pH values decrease, therefore, with an increase in the acid properties of the elements. Those elements which form hydroxides having a high isoelectric pH occur among the first groups in the periodic system, whereas the more acidic elements have a lower isoelectric pH. The elements in the center of the system yield hydrous oxides isoelectric near the point of neutrality.

TABLE 124

The $CeCl_4$ + NaOH system

A. 10 m.e. $CeCl_4$ in 1,000 cc.
B. 20 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	2.0	Clear	Clear	.....	....
20	4.0	Clear	xx	+3.0	....
20	5.0	Opal	xx	+2.5	....
20	5.2	Instant	xxxx	+0.7	6.4
20	5.5	Instant	xxxx	−0.7	7.1
20	5.7	Instant	xxxx	−1.0	8.0
20	6.5	Instant	xxxx	−3.0	9.8
20	8.0	Opal	xxxx	−3.8	10.2

Isoelectric at pH 6.75.

TABLE 125

The $Th(NO_3)_4$ + NaOH system

A. 10 m.e. $Th(NO_3)_4$ in 1,000 cc.
B. 10 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	14	Clear	xx	+1.5	6.2
20	15	Slow	xxx	+0.5	6.8
20	16	Instant	xxxx	−1.5	7.0
20	17	Instant	xxxx	−2.9	9.2
20	18	Rapid	xxxx	−3.0	9.8
20	19	Rapid	xxx	−3.0	10.0

Plus water to make total volume 50 cc. Isoelectric pH 6.85.

There are, however, irregularities in the electrokinetics of the hydrous oxides just as there are irregularities in the periodicity of the chemical properties of the elements. Thus, according to unpublished data by Hester and Mattson, copper in the first group and manganese in the seventh group yield, when $CuCl_2$ and $MnCl_2$ are precipitated by NaOH, hydroxides isoelectric at pH 7.6 and 7.05 respectively. These elements differ markedly also in their chemical

properties from the neighboring elements in the periodic system. The cataphoretic isoelectric point does not always express the acidic and basic properties that would be expected from the position of the elements in the periodic table, for reasons that will be discussed later.

TABLE 126

The $SnCl_4$ + NaOH system

A. 10 m.e. $SnCl_4$ in 1,000 cc.
B. 50 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	0.2	Instant	xxxx	+1.8	3.2
20	1.0	Instant	xxxx	+1.8	3.2
20	1.4	Instant	xxxx	+1.8	3.3
20	1.8	Instant	xxxx	+1.3	3.4
20	2.0	Instant	xxxx	+1.3	3.4
20	2.2	Instant	xxxx	+slow	3.5
20	2.5	Instant	xxxx	±0.0	3.9
20	3.0	Opal	x	−1.8	6.4

Plus water to make total volume 50 cc. Isoelectric pH 3.9.

TABLE 127

The $Pb(NO_3)_2$ + NaOH system

A. 10 m.e. $Pb(NO_3)_2$ in 1,000 cc.
B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	2.0	Rapid	xxxx	+1.5	9.4
20	2.5	Rapid	xxxx	+1.0	11.0
20	3.5	Instant	xxxx	+0.6	11.0
20	3.6	Instant	xxxx	−0.5	11.0
20	3.7	Instant	xxxx	−0.8	11.1
20	3.9	Instant	xxxx	−0.8	11.2
20	4.5	Slow	xxxx	−slow	12.0

Plus water to make total volume 50 cc. Isoelectric pH 11.0.

Cation adsorption and exchange

The hydroxides of stannic and stannous tin, titanium, aluminum, and ferric iron were prepared in bulk by precipitation from a normal solution of their respective chlorides at the isoelectric pH. They were removed from the mother liquor by filtration, but without washing, and to facilitate the work

TABLE 128

The $ZnCl_2$ + NaOH system

A. 10 m.e. $ZnCl_2$ in 1,000 cc.

B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	1.0	Clear	xxxx	+2.9	6.5
20	1.5	Slow	xxxx	+1.5	6.8
20	2.0	Instant	xxxx	+1.0	9.6
20	2.1	Instant	xxxx	±0.0	10.3
20	2.2	Instant	xxxx	−slow	10.3
20	2.4	Clear	xxxx	−0.3	11.0
20	3.0	Clear	x	.....	12.0

Plus water to make total volume of 50 cc. Isoelectric pH 10.3.

TABLE 129

The $MgCl_2$ + NaOH system

A. 10 m.e. $MgCl_2$ in 1,000 cc.

B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	3.0	Opal	xxxx	+1.5	9.6
20	3.5	Opal	xxxx	+1.5	9.6
20	4.5	Opal	xxxx	+1.5	10.0
20	5.0	Opal	xxxx	+1.4	10.9
20	10.0	Opal	xxxx	+slow	12.0

Plus water to make up to 50 cc. Isoelectric pH undetermined.

TABLE 130

The $CoCl_2$ + NaOH system

A. 10 m.e. $CoCl_2$ in 1,000 cc.

B. 50 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1/VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	1.5	Opal	xxxx	+2.0	8.0
20	2.0	Slow	xxxx	+1.5	8.2
20	3.0	Rapid	xxxx	+1.5	8.2
20	4.0	Rapid	xxxx	+1.5	9.2
20	5.0	Rapid	xxxx	+0.5	10.6
20	6.0	Rapid	xxxx	±slow	11.4
20	6.5	Rapid	xxxx	±slow	11.6

Plus water to make total volume 50 cc.

TABLE 131

Cation adsorption and exchange by isoelectrically precipitated hydroxides

HYDROUS OXIDES	ISOELECTRIC pH	EXCHANGEABLE Ba, M.E. PER GRAM AT pH 7	EXCHANGEABLE Ba, M.E. PER GRAM AT ISOELECTRIC pH OF COLLOID
Stannic	3.9	1.01	0.00
Titanium	4.8	0.84	0.00
Stannous	6.6	0.21	....
Ferric	7.1	0.00	0.00
Aluminum	8.1	0.00	0.00

TABLE 132

Adsorption of the oxalate ion by isoelectrically precipitated hydroxides

(Milliequivalents C_2O_4 per 0.5 gm. colloid)

HYDROXIDE	pH AT EQUILIBRIUM	C_2O_4 ADDED	C_2O_4 IN SUPERNATANT LIQUID	C_2O_4 ADSORBED
		m.e.	*m.e.*	*m.e.*
Ferric	6.0	1.70	1.167	0.533
	6.7	1.70	1.290	0.410
	7.1	1.70	1.352	0.348
	8.4	1.70	1.495	0.205
	8.8	1.70	1.546	0.154
	8.9	1.70	1.659	0.041
Aluminum	4.5	1.70	1.310	0.390
	7.2	1.70	1.284	0.416
	7.4	1.70	1.342	0.358
	8.2	1.70	1.361	0.339
	8.4	1.70	1.403	0.297
	8.7	1.70	1.485	0.215
	9.0	1.70	1.485	0.215
	9.2	1.70	1.536	0.164
Titanium	3.2	1.70	1.147	0.553
	6.6	1.70	1.454	0.246
	8.0	1.70	1.514	0.184
	8.2	1.70	1.556	0.144
Stannic	3.2	1.70	1.361	0.339
	3.6	1.70	1.413	0.289
	4.8	1.70	1.597	0.103
	8.6	1.70	1.699	0.001
Magnesium	9.4	1.70	1.680	0.020
	9.6	1.70	1.700	.....
	9.8	1.70	1.700	.....

they were dried at 65°C., and powdered. Their base exchange was determined at pH 7, and also at the isoelectric pH, by leaching with Ba-acetate until the pH of the leachate was equal to the pH of the original Ba-acetate solution. When the base exchange is determined with Ba-acetate at a pH corresponding to the isoelectric pH of the compound, the equilibrium is established immediately, but in order to make the two determinations comparable the leaching was continued until about 250 cc. of the solution had passed through the filter. Then 10 cc. of *N* $BaCl_2$ solution was added to the filter, and the compound washed free of chlorine. The adsorbed barium was displaced with hot *N*

TABLE 133

Adsorption of sulfate ion by isoelectrically precipitated hydroxides

(0.5 gm. colloid)

ISOELECTRIC HYDROXIDE	pH AT EQUILIBRIUM	SO_4 ADDED	SO_4 IN SUPERNATANT LIQUID	SO_4 ADSORBED
		m.e.	*m.e.*	*m.e.*
Magnesium	9.3	1.72	1.72	....
	9.5	1.72	1.72	....
	9.6	1.72	1.72	....
Ferric	3.3	1.72	1.08	0.64
	3.4	1.72	1.15	0.57
	4.0	1.72	1.24	0.48
	7.1	1.72	1.52	0.20
	7.2	1.72	1.52	0.20
Aluminum	4.2	1.72	1.23	0.49
	4.2	1.72	1.15	0.57
	4.4	1.72	1.23	0.49
	4.8	1.72	1.28	0.44
	6.8	1.72	1.34	0.38

NH_4Cl and the barium estimated gravimetrically as sulfate. The results are given in table 131.

The data demonstrate quite conclusively that those hydroxides that are isoelectric on the acid side of the neutral point possess the power to adsorb and exchange cations at pH 7.0, and that this capacity is greater the lower the isoelectric pH. Both tin and titanium hydroxide have an extremely high base exchange capacity, which is of the same order of magnitude as the various soil colloids and the amphoteric silicates, phosphates, and humates, having the corresponding isoelectric points (1, III). Aluminum and ferric hydroxides, isoelectric at or above pH 7.0, show only a negligible cation adsorption at this pH.

If the pH of the barium acetate is adjusted to the isoelectric pH of the colloid no trace of barium exchange is obtained, so that for these hydroxides at least there is no cation exchange if the colloid is leached with a solution the pH

of which corresponds to the isoelectric pH. With soil colloids, however, a small degree of cationic exchange is always observed under similar conditions (1, V), an overlapping of both cationic and anionic adsorption taking place at the isoelectric pH, so that the common anions are adsorbed slightly at a pH above the isoelectric pH of the colloids, and the common cations to a small extent below this point, the extent to which the exchange of both anions and cations overlap at the isoelectric point being greater the more strongly adsorbed or the least dissociated the ions.

ANION ADSORPTION

While the cationic adsorption was studied under leaching conditions, so that the reaction is thrown in one direction by removal of the acetic acid formed, the study of anion adsorption was done under equilibrium conditions, and the oxalate ion in these preliminary experiments was found to be very suitable. Half-gram portions of the dried isoelectrically precipitated hydroxides were allowed to come to equilibrium over a 24-hour period with a 100-cc. solution containing 1.70 m.e. of oxalate. Variations in pH were obtained by altering the amounts of oxalic acid or ammonium oxalate used, both of the same concentration, so that the oxalate concentration was maintained constant. The pH values above the neutral point were obtained by the addition of ammonia. The results obtained with aluminum, titanium, ferric, and stannic hydroxides are shown in table 132, and are graphically represented in figure 38.

Within the pH range where all the four colloids remain insoluble and coagulated, the adsorption of oxalate is greatest by that hydroxide which has the highest isoelectric point, whereas the adsorption of barium increases in the reverse order. The adsorption of anions increases with a decrease in pH, whereas the adsorption of cations increases with increasing pH from the isoelectric pH.

Apart from the distinct correlation between the isoelectric pH and the adsorption of ions, the actual magnitude of the adsorption has in this connection no great significance, because of the considerable solubility effects that are introduced. Aluminum hydroxide at the lowest pH (4.5) adsorbs less oxalate than at the next pH, which must be due to the solubility of the compound formed on adsorption. Other factors also influence the degree of adsorption, such as aging and the degree of polymerization of the molecules that constitute the ionic micells.

Magnesium hydroxide, a strongly basic compound, fails to show a trace of adsorption at any pH, the oxalate ion apparently being too highly dissociated to displace the OH ion, which on the alkaline side suffers a suppressed dissociation.

The adsorption of the sulfate anion was determined with iron, aluminum, and magnesium hydroxides. Sodium sulfate and sulfuric acid, of the same con-

centration were used, variation in pH being introduced by varying the proportion of sodium sulfate and sulfuric acid. The results are shown in table 133.

Again magnesium hydroxide failed to show any anion adsorption, presumably because this ion is too highly dissociated and the compound too soluble. The aluminum and ferric hydroxides adsorb sulfate to a considerable extent, as was expected from previous work on the isoelectric precipitation of

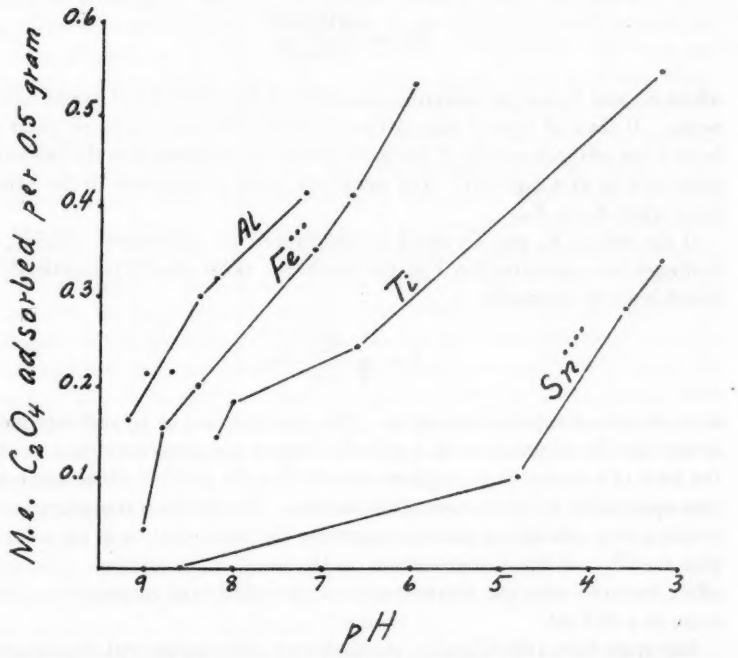


FIG. 38. THE ADSORPTION OF THE OXALATE ION BY ALUMINUM (8.1), FERRIC (7.1), TITANIUM (4.8), AND STANNIC (3.9) HYDROXIDES

(The figures in parenthesis give the isoelectric points of the hydroxides when precipitated from the chlorides.)

ferric and aluminum hydroxides prepared from the corresponding sulfates (1, III).

GENERAL DISCUSSION

On the basis of the theory of colloidal electrolytes largely developed by Michaelis (2), ampholytoids are to be regarded as colloids that dissociate both cations and anions and, conversely, adsorb both cations and anions depending on the conditions. An equilibrium exists between the ions and the undissociated micellae, just as exists between smaller ions in an ordinary electrolyte.

If the undissociated molecule is represented as HROH, it can dissociate in two ways, in the first place as an acid according to the equation:

$$K_a = \frac{(\mathrm{ROH})(\mathrm{H})}{\mathrm{HROH}} \qquad (A)$$

and then as a base according to the equation:

$$K_b = \frac{(\mathrm{HR})(\mathrm{OH})}{\mathrm{HROH}} \qquad (B)$$

where K_a and K_b are the ionization constants of the acidoid and basoid components. If the acid type of dissociation predominates, the isoelectric point will be at a low pH; conversely, if the basic ionization predominates the isoelectric point will be at a high pH. The isoelectric point corresponds to the neutral point when $K_a = K_b$.

If the values K_a and K_b could be determined for amphoteric colloids, the hydrogen-ion concentration I at the isoelectric point should theoretically be found from the expression

$$I = \sqrt{\frac{K_a}{K_b} \cdot K_w}$$

as in the case of soluble electrolytes. We cannot, however, by ordinary means determine the dissociation of a colloid, because the dissociated ions exist in the form of a swarm or atmosphere surrounding the particle whose concentration apparently increases toward the surface. The hydrion concentration we measure in a colloidal suspension represents the concentration in the solution, plus the effect of the dissociated ions in the micellar atmosphere. The latter effect increases with the concentration of the colloid and approaches a maximum in a stiff gel.

But apart from this difficulty, the isoelectric point varies with the nature of the anion adsorbed, being very often different for each compound. Although the amphoteric soluble electrolytes such as the amino acids have a well-defined isoelectric point which is independent of the nature of the salt used for determining it, the different compounds formed by replacing the hydroxyl ion in a colloid by another ion will often have a new isoslectric pH. In colloids it is not only the H and OH ions which are slightly dissociated, but all other ions dissociate to a limited extent. Dissociation can proceed only until a certain critical potential is established, and in a highly multivalent complex this requires a comparatively small number of ions (1, II). Dissociation beyond this point must result in an increased dispersion, and a complete dissociation will lead to an ultimate dispersion reaching the molecular stage, in which case the material ceases to be a colloid.

An amphoteric colloid whose $K_a > K_b$ must in the free condition have an acid reaction and be negatively charged, since the H ions are more dissociated

than the OH ions. To render the colloid isoelectric, acid must be added to suppress the dissociation of the acid group and increase that of the basic group. The complex will be *isoionic* when the dissociation of its cations and anions are equal but it might not thereby become isoelectric.

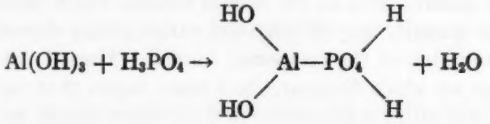
In the case of soluble ampholytes which form *completely dissociated* salts the quantity of acid required is always very small, and theoretically independent of its nature. But in the case of colloids which undergo a *limited dissociation* the quantity may be large and varies greatly depending upon the degree of dissociation of the compound formed. Thus if the OH ions are displaced by an ion which dissociates to a lesser degree than the former there can be no gain but rather a diminution in the positive charge, and the complex cannot become isoelectric. It might be assumed that, if the pH be lowered sufficiently, the colloid, in spite of this, will become isoelectric and finally electropositive as a result of a suppression of the hydrion dissociation. This is not necessarily the case, however, for all inert colloids charge themselves electronegatively in water, and this residual negative charge must be balanced by a certain degree of anionic dissociation before the colloid can be isoelectric. If, therefore, the anions be very slightly dissociated, the colloid, although it be amphoteric and in its isoionic condition, may not become isoelectric but remain electronegative, or it may show an isoelectric point considerably below its isoionic point. This might account for the fact that the fairly strong bases of divalent Cu and Mn were found isoelectric at pH values as low as 7.6 and 7.05 and that Bi stays electronegative in spite of its strong basic and faintly acidic nature.

The low dissociation of Cl ions from bismuth oxychloride probably accounts for the fact that this compound remained electronegative down to pH 2.8, whereas antimony trioxide was found to be isoelectric at pH 5.6. From this, one should have expected bismuth to have a still higher isoelectric point, since the element is the more basic of the two (3).

That the isoelectric point of "hydroxides" varies with the nature of the anion in combination has previously (1, III) been shown in the case of aluminum and iron. Aluminum hydrous oxide precipitated from the chloride by the addition of NaOH was isoelectric at pH 8.1, and had a composition expressed by the formula $(Al_2O_3)_{416} \cdot Al_2O_2Cl_2$, whereas the sulfate yielded a compound isoelectric at pH 7.6 and with the composition $(Al_2O_3)_{12.6} \cdot Al_2O_2SO_4$. The difference in the isoelectric points as well as in composition must be ascribed to a difference in dissociation, the SO_4 ions obviously being less dissociated and displacing a greater number of OH ions than the Cl ions. The phosphate ion caused a still greater deflection of the isoelectric point toward the acid side, a compound of the composition $Al_2O_3 \cdot (P_2O_5)_{0.86}$ being isoelectric at pH 4.9. It is not the hydroxide which is isoelectric at different pH values but a complex whose composition varies constantly with a change in reaction and the ionic environment in general. This change in composition is the most potent factor in causing a change in the electrokinetic behavior and chemical properties. It

not only alters the dissociation of the acid and basic groups but very often adds new groups or inactivates those already present. In this way the acid group may be strengthened and the basic group weakened or vice versa.

Thus if the OH ions be displaced by a polybasic acid such as H_3PO_4 a new acid group may be introduced whereas the basic group has been weakened according to the following equation:



If the union between Al and PO_4 results in a practically non-dissociated compound, it is clear that the dissociation of the basic group has been permanently reduced. In addition there has been introduced an acid residue which adds greatly to the acid dissociation of the colloid. This explains the lowering of the isoelectric point and the increase in the cation exchange capacity observed in the case of phosphated, silicated, and humated sesquioxides (1, V).

The precipitation of the amphoteric hydroxides may be illustrated as follows:

$$Al^{+++} \rightarrow AlOH^{++} \rightarrow Al(OH)_3^{+} \text{ etc.}$$

With decreasing dissociation, and decreasing colloidal dispersion, a floc with the following formula may be formed:

$$[Al(OH)_3]_x \cdot [Al(OH)_3]_z^{+} + zCl^{-}$$

In this scheme the value of x is assumed to increase in the direction of the isoelectric point. It is obvious that we have every transition in dispersion and charge all depending upon the degree of dissociation. When the charge of a particle falls below a certain critical value an association of two or more particles results until the ionic density and charge is again such as to maintain a stable condition. There is no discontinuity between the "crystalloid" and colloid conditions of matter; the one merges imperceptibly into the other.

The extension of the zone of flocculation and therefore the degree of dispersion depend upon the dissociation of the diffusible ions in combination. Ca and SO_4 ions in combination with most ampholytoids are less dissociated than Na and Cl ions. The former give, therefore, a wider zone of flocculation.

Since the ampholytoids are weak acids and bases, their salts all undergo more or less extensive hydrolysis, and, since the diffusible ions can be removed by leaching, dialysis, and electrodialysis, these processes all lead to the unsaturated condition, the pH thereby changing in the direction of the isoelectric point. An amphoteric colloid is most easily "purified" at the isoelectric point. This is taken advantage of in analytical chemistry. Thus stannic acid is precipitated for gravimetric estimation by precipitation with ammonia, to the methyl orange end point (pH 3.1 – 4.4), whereas the isoelectric pH of the

compound is about pH 3.9. Ferric and aluminum hydroxides isoelectric when precipitated from their chlorides at pH 7.1 and 8.1 respectively are precipitated with ammonia at about the neutral point. At the isoelectric point (or perhaps more strictly at the isoionic point) the dissociation of an amphoteric compound is at a minimum and the cationic and anionic dissociations are equal. An amphoteric colloid is therefore least soluble, least dispersable, and most stable at the isoelectric (or isoionic) point. These are the fundamental principles which form the basis of the theory of isoelectric weathering (1, IX).

SUMMARY

This paper deals with the isoelectric point and ionic exchange of a number of hydrous oxides.

A general relationship is observed between the position of the isoelectric point and the acidic or basic properties of the elements. Their electrokinetic behavior, however, is not always indicated by their position in the periodic table, apparently because of differences in dissociation of the various compounds and of the fact that the isoelectric point does not coincide with the isoionic point.

The hydrous oxides isoelectric below pH 7.0 adsorb and exchange cations at this pH, a capacity which increases as the isoelectric pH decreases. The adsorption of anions increases with diminishing pH, in the reverse order to cationic adsorption.

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LAWS OF SOIL COLLOIDAL BEHAVIOR: III. COLLOIDAL PHOSPHATES[1]

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Previous investigations by Mattson have shown that the colloidal materials of soil and other colloids divide themselves electrokinetically into positive and negative colloids, depending to a considerable extent on the pH of the medium, the composition of the colloid, and the ratio of $\frac{\text{acidoid}}{\text{basoid}}$.

Positive and negative colloids mutually flocculate each other, forming new compounds, the ionic exchange capacity of which vary with the composition and the position of the isoelectric point with respect to the pH. Different ions enter the micelle and form part of the molecule, and with this difference in composition there will be a difference in the degree of dispersion and solubility at any pH. This variation in physical properties with composition gives rise to the development of horizons in soils. Hydrolysis of the soil and dispersion of the particles take place in one layer, followed by migration of the dispersed particles through the soil to another layer where, because of differences in pH, the particles again combine and flocculate.

In several publications by Mattson (13) the isoelectric precipitations of a large number of compounds were recorded. In the present work this study has been extended to include a fairly complete range of phosphate compounds that may arise in the soil by hydrolysis or by addition in the form of fertilizers.

EXPERIMENTAL

Accurately measured portions of the two solutions A and B to be mixed were placed in separate tubes, and sufficient water was added to make the total volume 50 cc. The variation in pH was introduced by adding HCl or NaOH, the HCl being added to the salt solutions and the NaOH to the phosphate solutions.

[1] Editor's note: Papers I and II of Pugh's series "Laws of Soil Colloidal Behavior" were erroneously included in Mattson's series "Laws of Soil Colloidal Behavior" as papers XIV and XV (SOIL SCIENCE 37: 403; 38: 161).

Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

[2] The author desires to thank Dr. Sante Mattson for suggesting this problem and for his advice during the progress of the work. Thanks are also due to the British Ministry of Agriculture for a research scholarship during the tenure of which this work was carried out.

The flocculation after the solutions were mixed and after they were allowed to stand overnight are recorded in the tables. The latter is represented by the usual notation of x signifying slight, xx about half complete, xxx nearly complete, and xxxx complete flocculation. The phosphate in the supernatant liquid was determined either by the Fiske and Subbarow (8) or by the Deniges (7) method, and the pH by the quinhydrone electrode or colorimetrically. Cataphoresis measurements were made on the remaining suspensions.

STRUCTURE OF PHOSPHATES

Phosphatic compounds are frequently represented as double salts or molecular compounds with a formula such as $Ca_3P_2O_8 \cdot Ca(OH)_2$. Although justification for such a formulation could hardly be obtained, the use of such formulas became general because at the time there was no other adequate theory which could displace the older conception, until Werner introduced his theory of co-ordination. With the development of the theories of atomic structure and of valency by Bohr (2), Bury (4), Lewis (10), and Sidgwick (19), a reasonable explanation for the existence of the co-ordination compounds of Werner was obtained by Lewis. These theories (16) have been applied in a previous paper to interpret the phenomena of aging in colloids with aluminum hydroxide and silicate. The same theory can be applied to phosphates and is rendered necessary in order to explain the nature of the reaction that takes place in a colloidal micelle with a differentiation in the hydrogen-ion concentration of the liquid phase.

The recent advances in the development and interpretation of base exchange reactions were made possible because of the recognition that the hydrogen ion at the surface of the colloidal anion takes its part with other cations in exchange reactions. Although the position of the hydrogen ion is thus moderately well defined, the part played by the hydroxyl ion is uncertain and has not been the subject of extensive investigation, because in ion exchange reactions, as in most surface reactions, peculiarly little attention has been paid to the composition of the colloidal anion. It is in the latter respect that the hydroxyl ion becomes the dominating ion, and it is with that purpose in view that this preliminary work on phosphates has been done.

The influence of pH on the adsorption of ions by hydroxides (16) showed that at a pH below the isoelectric pH of the colloid, there was exchange alkalinity, that is, a hydroxyl ion entered the solution as the anion, whether sulfate or oxalate, entered the colloid. Such an adsorption is obviously a pronounced exchange reaction, of the same nature as base exchange, and it proceeded without any obvious alteration in the physical properties of the colloidal micelle over a considerable pH range. In the preparation of these phosphate compounds, it was also observed that as the hydroxyl ion exceeds a certain concentration, the PO_4 ion is being replaced by the hydroxyl group, and the ratio of $\frac{P_2O_5}{R_xO_y}$ is diminished as the pH is increased, but the solubility and physical

properties of the micelle are not altered by the change. Thus with stannic phosphate at pH 2.2, the molecular ratio of $\frac{SnO_2}{P_2O_5}$ is 6.2, but at pH 3.75 it is 12.40.

Representing phosphates as molecular compounds does not permit of an explanation of such an exchange, but an analogous phenomenon takes place in the Werner compounds where a whole group such as NH_3 can be replaced by a simple atom like chlorine. Nitrogen, atomic structure (2) (5),[3] combines with three hydrogen atoms each with a lone valence electron, and by sharing of electrons it reaches the stable number of neon (2) (8), and hydrogen the stable number of helium (2), thus

$$\begin{array}{c} H \\ \cdot\cdot \\ H:\underset{\cdot\cdot}{N}:H \end{array}$$

This leaves the nitrogen of the ammonia with a lone pair with which it can combine with another atom thus forming a co-valent bond. A characteristic change of electrovalency accompanies substitution in the co-ordination zone. Thus,

$$\left[\begin{matrix} Pt(NH_3)_3 \\ Cl_2 \end{matrix}\right]$$

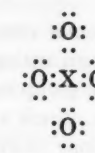
If a neutral chlorine atom is removed, it will take with it one of the pair of electrons which it previously shared with the platinum, and the other is left behind. If now the ammonia molecule takes its place, this provides the two electrons necessary for the attachment, so that platinum has gained one electron by the exchange. It had already in the original compound the requisite number of electrons for stability, but it has now one too many. It will lose this to the displaced chlorine atom forming an electrovalency, and a salt $\left[\frac{Pt(NH_3)_3}{Cl}\right]$ Cl is formed.

In the complexity of their composition, colloids show many similarities in properties to Werner compounds, but have as well other properties due to the presence of a hydroxyl group, and in particular of the hydrogen ion that arises during dissociation, for the strong adsorption of this ion must be attributed to the ease with which it can form a co-valency with a lone pair of electrons, and its high mobility due to its small volume.

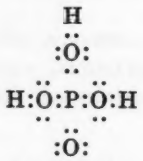
Phosphorus with atomic number (15) and electronic structure (2) (8) (5) acts both as a trivalent and as a quinquevalent element. It can combine with three hydrogen atoms, and, by sharing the valency electrons, reach the stable number of argon (18) with the formation of PH_3. Arising out of the electronic conception of valency, a very interesting formulation of phosphoric acid H_3PO_4

[3] The number in parenthesis immediately following the name of the element refers to its atomic number or electronic arrangement.

was suggested by Lewis. A co-ordinate co-valency arises out of one atom contributing both of the electrons that form a single link. With the oxy-acids of the type H_nXO_4 the eight shared electrons in the ion

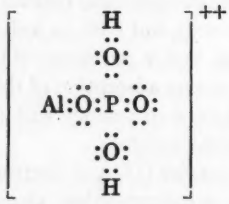


are all needed to make up the valency electrons of the oxygen (2) (6) from six to eight and must be derived from the central atom or outside. If X is phosphorus with five valence electrons to start with, it will require three more, which it obtains from three hydrogen atoms with the formation of H_3PO_4.



The formulation of phosphoric acid in this way gives to phosphorus a maximum co-valency of four, a group of eight shared electrons. There is no doubt that with a large number of compounds the maximum co-valency is four, but with PCl_5 its maximum co-valency is five, a group of ten shared electrons.

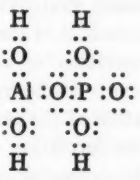
The formation of aluminum phosphate from aluminum chloride and phosphoric acid can be represented as follows. Aluminum, atomic number (13) and electronic structure (2) (8) (3), gives an electron to each chlorine atom (2) (8) (7). In solution these dissociate, and the chlorine takes away the bonding pair of electrons. The phosphoric acid combines through the lone pair of an oxygen atom forming the ion



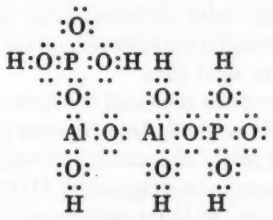
This saturates one valence of the aluminum, whereas a co-valency of three could be satisfied by a greater dissociation of the phosphoric acid, with three oxygen atoms of the PO_4 ion combining with the aluminum through their lone pairs. The hydroxyl, phosphoric acid, silica, and also chlorine ions can enter simultaneously, depending on the maximum co-valency formation that the

aluminum is capable of achieving, and the fact that the proportion in which each of them would contribute to the saturation of the central atoms would be determined by the law of mass action and the stability of each co-valency. In the present work this has not been investigated because only the pH and not the concentration of hydroxyl ions has been determined.

The formation of a colloidal micelle with phosphates can take place in the same way as with aluminum hydroxide and silicate, by continuous polymerization of the molecules. If we represent a phosphate in the original molecular stage as



only the first dissociation of phosphoric acid into H^+ and $H_2PO_4^{--}$ is assumed. If now the hydrogen wanders from the hydroxyl group of this molecule, then the whole molecule can combine, through the lone pair of the oxygen, with another molecule, by the oxygen from which the hydrion has left giving its lone pair of electrons toward the saturation of the aluminum. This, as with hydroxides and silicates (16), leads to indefinite polymerization, the valency of the aluminum increasing from three to four, and the internal central atom becomes saturated, but the whole micelle or giant molecule will be capable of indefinite polymerization because of the unsaturation of the surface aluminum atom. The molecule would have the following hypothetical structure:



With complete dissociation of the phosphoric acid, three oxygen atoms of the trivalent PO_4 ion would give their lone pair of electrons toward the saturation of the central atom.

Just as the substitution of chlorine for ammonia is rendered possible in Werner compounds, by the fact that the ammonia has a lone pair of electrons and can replace the chlorine bond unit by unit, so in phosphates the hydroxyl ion $:\ddot{O}:H$, with the "lone pair" of the oxygen, can displace the bond formed by the oxygen of the phosphoric acid. As long as only a small percentage of the

phosphoric acid is thus replaced, it is probable that too great a variation in the physical properties of the micelle is not produced by the substitution, which could thus proceed within certain limits of pH. Too high a concentration of hydroxyl ions would, however, introduce hydrolysis at the central bonds, with the possible secondary effects of dispersion and solubility. The number of hydroxyl ions required to displace the surface phosphoric acid will depend on the number of oxygen atoms that combine with the central atom. If all the bonds are utilized, then three hydroxyl groups would be required to displace a PO_4 group.

Mattson (13) has demonstrated that phosphates have a lower isoelectric pH than the corresponding hydroxides of the metal. For the synthesis of the ionic micelle a certain concentration of anions, whether hydroxyl ion or phosphoric acid ions, is necessary. If the hydroxyl ion is the only anion that contributes towards the saturation of the central atom, then a comparatively high pH will be required for the formation of the micelle. If other ions are added that can contribute to the saturation of the central atom, then a micelle will be formed at a lower pH, but a certain concentration of hydroxyl ions is necessary in all cases in order to prevent acid hydrolysis.

The linkages formed between the phosphoric acid, hydroxyl ions, and the central atom, where the bonding pair of electrons come from one and the same atom, are thus in all cases co-ordinate co-valency bonds. From the viewpoint of colloid chemistry the properties of compounds with co-ordinate co-valent linkages that are of importance are: (*a*) They have an open structure and occupy a large volume as compared with simple crystals, e.g. sodium chloride; (*b*) Compared with compounds containing electrovalent bonds they exhibit considerable stability; (*c*) The forces are directed forces that proceed from atom to atom, and form an integral part of the constitution of each molecule, whereas in those compounds with electrovalencies the forces are from ion to ion, and a stable chemical bond is not achieved, for unlike co-valent compounds they are ionized even in the solid state.

A question that remains to be answered is whether on suspension in water the non-dissociated portion is wholly held together by electrovalent links, or whether it forms ions and partly dissociated co-valent molecules. The whole phenomenon of ion exchange as investigated by Mattson (13) and for hydroxides by the author, point to the latter conclusion. The phenomenon of ion exchange is due to the dissociation of hydrions or hydroxyl ions from the surface of the amphoteric colloids, which leaves the main body of the micelle untouched and still in the co-valent form. At the isoelectric point the dissociation is at a minimum, but its position with respect to the pH is a function of the specific properties of the colloid, that is, its strength as an acid or base. In the unsaturated condition the surface of the micelle consists of hydroxyl groups, and the pH of the salt solution used to determine the ion exchange alters both the degree and the nature of the dissociation due to mass action. In terms of atomic structure the ratio of the co-valent to the electrovalent form

is a maximum at the isoelectric point, that is, the dissociation is least, and since ion exchange can take place only as a secondary reaction to dissociation, the ion exchange is a minimum when the colloid is treated with a solution the pH of which corresponds to the isoelectric pH.

The dissociation of hydrions or hydroxyl ions from the surface of a phosphatic micelle will, as in the case of a soil, give ion exchange reactions, subject to the limitations imposed by the position of the isoelectric point with respect to the pH. The fact that Mattson (13) found that iron and aluminum phosphates have considerable base exchange capacity at pH 7, proves this to be true. The formulation of phosphates in this manner, although as yet indefinite, is

TABLE 1

The $SnCl_4$ + Na_2HPO_4 system

A. 20 cc. of $SnCl_4$ solution (10 m.e. SnO_2 per liter)
B. 20 cc. of Na_2HPO_4 (2.42 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	0.492	Rapid	xxxx	— slow	2.10	1.56	0.86
.....	0.246	Rapid	xxxx	— slow	2.30	1.58	0.84
0.027	.....	Rapid	xxxx	— slow	2.83	1.67	0.75
0.123	.....	Rapid	xxxx	— slow	3.32	1.74	0.68
0.148	.....	Rapid	xxxx	— slow	4.11	1.85	0.57
0.197	.....	Clear	Clear	.....	7.00	....	....

200 cc. $SnCl_4$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	SnO_2 ADDED	SnO_2 IN SOLUTION	SnO_2 IN PRECIPITATE	P_2O_5 IN SOLUTION	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{SnO_2}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
2.19	75.6	Trace	75.6	15.50	8.70	6.19
2.40	75.6	Trace	75.6	16.87	7.33	9.73
3.75	75.6	Trace	75.6	18.01	6.19	12.40

more reasonable than an assumption of the existence of a molecular compound, but because of the lack of precise information no hypothetical formula is attempted, but the composition of each is discussed in its bearing on soil problems.

Stannic and titanic phosphates

The quantity of phosphate, the pH of precipitation, and the cataphoretic mobilities of stannic and titanic phosphate precipitates are shown in tables 1 and 2. Stannic phosphate has no isoelectric point at any finite pH, the acid-dissociation being much too strong, whereas titanium has an isoelectric point at a low pH. The quantity of phosphate adsorbed is very small but definite.

In acid solutions both are very stable, but are dispersed at pH 6.0. Tin does not exist in the colloid fraction of the soil, but titanium does in small quantities of about 1 per cent TiO_2, as found in the colloid fractions investigated by Robinson and Holmes (17), and by Byers, Anderson, and Brown (3, 5). Upon acid extraction of a soil, a part of the phosphate will be retained in insoluble form by combination with titanium. Ward (20), found it necessary, with Hawaiian soils, to fuse with Na_2CO_3 the residue after acid extraction in order to obtain all the phosphate, because of the unusually high percentage of titanium that these soils contain, with the precipitation of phosphate in strongly acid solutions.

TABLE 2

The $TiCl_4$ + Na_2HPO_4 system

A. 20 cc. of $TiCl_4$ solution (10 m.e. TiO_2 per liter)
B. 20 cc. of Na_2HPO_4 solution (2.42 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	0.197	Rapid	xxxx	.....	2.40	1.61	0.81
.....	.....	Rapid	xxxx	+ slow	2.80	1.61	0.81
0.098	.....	Rapid	xxxx	−1.51	3.35	1.72	0.70
0.123	.....	Rapid	xxxx	−2.02	3.71	1.72	0.70
0.137	.....	Rapid	xxxx	−3.03	4.82	2.08	0.34
0.148	.....	Turbid	Turbid	.....	6.28	....	....

200 cc. $TiCl_4$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	TiO_2 ADDED	TiO_2 IN SOLUTION	TiO_2 IN PRECIPITATE	P_2O_5 IN SOLUTION	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{TiO_2}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
2.37	40.0	Trace	40.0	19.04	5.16	13.6
2.92	40.0	Trace	40.0	19.04	5.16	13.6
3.80	40.0	Trace	40.0	20.20	4.00	17.7

Ferric and aluminum phosphates

Ferric and aluminum phosphates have previously been investigated by both Mattson (13) and Gaarder (9). The results obtained with these phosphates at three different concentrations of phosphate, keeping the bases constant, are shown in tables 3 to 7.

The zone of precipitation of ferric and aluminum phosphates, with respect to the pH, extends much more to the acid side than with the hydroxides alone. The phosphates also have a lower isoelectric pH than the corresponding hydroxides.

With increasing pH, the amount of phosphate in the precipitates diminishes,

TABLE 3

The $FeCl_3$ + Na_2HPO_4 system

A. 20 cc. of $FeCl_3$ (10 m.e. Fe_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (2.42 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		Immediate	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.123	.....	Clear	Clear	.....	4.23	....	....
0.128	.....	Rapid	xxxx	+ slow	4.78	0.06	2.16
0.133	.....	Rapid	xxxx	−1.51	5.18	1.00	1.42
0.138	.....	Rapid	xxxx	−1.89	5.85	1.00	1.42
0.143	.....	Clear	Clear	.....	6.31	....	....

200 cc. $FeCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Fe_2O_3 ADDED	Fe_2O_3 IN LIQUID	Fe_2O_3 IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{Fe_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
5.6	53.2	Trace	53.2	Trace	24.20	1.95
6.2	53.2	Trace	53.2	0.92	23.28	2.03
6.4	53.2	Trace	53.2	1.85	22.35	2.11

TABLE 4

The $FeCl_3$ + Na_2HPO_4 system

A. 20 cc. of $FeCl_3$ (10 m.e. Fe_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (9.68 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		Immediate	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	0.148	Turbid	xxxx	+ rapid	2.85	4.90	4.78
.....	0.074	Opal	xxxx	+2.02	3.33	5.26	4.42
.....	0.010	Rapid	xxxx	+0.60	3.79	5.26	4.42
.....	.....	Opal	xxxx	−1.01	3.80	5.26	4.42
0.020	.....	Clear	x	.....	4.90	....	....

200 cc. $FeCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Fe_2O_3 ADDED	Fe_2O_3 IN LIQUID	Fe_2O_3 IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{Fe_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
2.6	53.2	Trace	53.2	46.75	50.05	2.41
3.6	53.2	Trace	53.2	50.00	46.80	2.58
4.6	53.2	Trace	53.2	51.29	45.51	2.65

TABLE 5

The $AlCl_3 + Na_2HPO_4$ system

A. 20 cc. of $AlCl_3$ (10 m.e. Al_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (2.42 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	Flocculation		μ/sec. 1 volt/cm.	pH	P_2O_5 in supernatant liquid	P_2O_5 in precipitate
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.118	.....	Clear	Clear	.....	....	.....	....
0.129	.....	Opal	Opal	.....	5.58	.....	....
0.132	.....	Rapid	xxxx	±0.00	6.10	0.083	2.14
0.138	.....	Rapid	xxxx	− slow	6.51	0.620	1.80
0.143	.....	Clear	xxxx	− slow	6.65	0.670	1.75
0.148	.....	Clear	x	− rapid	7.00	.....	....

200 cc. $AlCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Al_2O_3 added	Al_2O_3 in liquid	Al_2O_3 in precipitate	P_2O_5 in liquid	P_2O_5 in precipitate	Mol. ratio $\frac{Al_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
6.1	34.10	4.2	29.90	0.53	23.67	1.75
6.6	34.10	2.8	31.30	2.45	21.75	1.99

TABLE 6

The $AlCl_3 + Na_2HPO_4$ system

A. 20 cc. of $AlCl_3$ (10 m.e. Al_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (4.84 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	Flocculation		μ/sec. 1 volt/cm.	pH	P_2O_5 in supernatant liquid	P_2O_5 in precipitate
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.069	.....	Clear	Clear	.....	4.75	....	....
0.079	.....	Rapid	xxxx	+2.75	5.01	0.53	4.31
0.089	.....	Rapid	xxxx	+1.51	5.33	1.23	3.61
0.099	.....	Rapid	xxxx	±0.00	6.11	1.45	3.39
0.109	.....	Slow	xxxx	− slow	6.38	2.85	1.99
0.119	.....	Clear	Clear	.....	7.50	....	....

200 cc. $AlCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Al_2O_3 added	Al_2O_3 in liquid	Al_2O_3 in precipitate	P_2O_5 in liquid	P_2O_5 in precipitate	Mol. ratio $\frac{Al_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
5.0	34.10	1.4	32.7	11.57	36.83	1.23
6.4	34.10	5.2	28.9	17.24	31.16	1.29

the hydroxyl ion replacing the PO_4. Both acid and alkaline hydrolysis occurs, and there is an optimum pH at which these compounds can be precipitated. This is about the isoelectric pH, but flocculation extends to both sides. The quantity of phosphate adsorbed in the precipitate need not be a maximum at the isoelectric pH, for both OH and PO_4 ions enter into the structure of the ionic micelle, and which predominates at the isoelectric point is not known. Under natural conditions, the soil colloid by hydrolysis goes through a structural re-arrangement so that its composition will correspond to its isoelectric pH, as has been found to be the case by Mattson (13).

TABLE 7

The $AlCl_3$ + Na_2HPO_4 system

A. 20 cc. of $AlCl_3$ (10 m.e. Al_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (9.68 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	0.010	Clear	Clear	.....	4.45	....	....
0.005	0.000	Rapid	xxxx	+0.81	5.01	5.51	4.17
0.010	0.000	Rapid	xxxx	+0.76	5.47	5.66	4.02
0.015	0.000	Rapid	xxxx	−0.76	5.53	5.66	4.02
0.020	.....	Rapid	xxxx	−0.84	5.93	5.66	4.02
0.030	.....	Slow	xxxx	−1.51	6.41	5.66	4.02
0.040	.....	Clear	Clear	.....	7.00	....	....

200 cc. $AlCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Al_2O_3 ADDED	Al_2O_3 IN LIQUID	Al_2O_3 IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{Al_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
4.9	34.10	Trace	34.10	52.21	44.59	1.00
5.2	34.10	Trace	34.10	54.05	42.75	1.11
6.4	34.10	Trace	34.10	57.80	39.00	1.22

Calcium and magnesium phosphates

An apparent difficulty arises with calcium and magnesium phosphates if they are represented as was the aluminum phosphate, on the basis of atomic structure and the modern conception of valency. Magnesium, atomic number (12) and electronic structure (2) (8) (2), combines with chlorine to give a highly dissociated compound. Calcium, atomic number (20) and electronic structure (2) (8) (8) (2), does the same. That this type of structure is highly dissociated was taken as evidence, in the work on aging of colloids, that in base exchange, at the surface of the particle, the magnesium and calcium could be held only by electrostatic attraction, the bond (2) (8) (2) not being a true bond.

A different viewpoint can, however, be obtained if the calcium and magne-

sium be regarded as the central atom. In a soil particle swathed with a water medium, since the solution contains very little silica, phosphate, or any of the polyvalent anions, the only anion is the giant polyvalent anion of the soil itself, the surface exchangeable bases being added after the polymerization of the colloidal micelle was complete. Both calcium and magnesium form the compounds $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ in the solid form, which on Werner's theory would be represented somewhat as follows:

$$\begin{bmatrix} H_2O & & H_2O \\ H_2O & Ca & H_2O \\ H_2O & & H_2O \end{bmatrix} Cl_2$$

Magnesium has a much greater tendency to take on the co-valent form than calcium, which it does in the Grignard reagent with ether:

$$(C_2H_5)_2O \rightarrow Mg(OH)(I) \leftarrow (C_2H_5)_2O$$

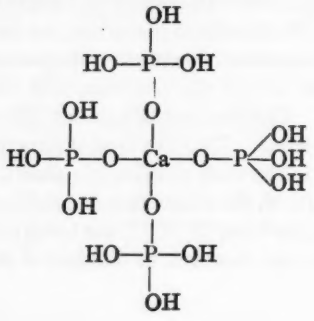
where the magnesium has a group of eight shared electrons, a co-valency of four, the ether being the "donor molecule," that is, the one that gives the extra electrons to the magnesium.

With both $CaCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ an analogous situation arises. Water has the remarkable property of associating, that is, one simple molecule combining with another simple molecule to form a chain as follows:

$$\begin{array}{ccccccc} H & - & O & - & H & - & O - \\ & & | & & & & | \\ & & H & & & & H \end{array}$$

This is a molecule in which the end oxygen has a lone pair of electrons or a single bond which is not utilized in combination. It has also a di-valent hydrogen which renders it unstable so that it can break easily into simple H_2O units.

This is the possible cause of hydration of ions on chemical grounds. In the formation of calcium and magnesium phosphates an analogous reaction may occur, the central atom, as with aluminum, taking on a very high co-valency of 4 or 6, forming as before a highly polymerized molecule, and ultimately a micelle, which could be represented simply as:



The surface hydrogen, that of the hydroxyl group, is the one that dissociates and is replaced by calcium or magnesium if present in excess. A combination like this, however, is probably stable only in the presence of considerable excess of anions, either hydroxyl or phosphate, and the phosphates of both calcium and magnesium are precipitated at a high pH.

As with the phosphates of the other elements, the phosphates of both calcium and magnesium show a variation in composition with pH and with increased concentration of phosphate, as shown in tables 8 to 13. Magnesium phosphate

TABLE 8

The $CaCl_2$ + Na_2HPO_4 system

A. 20 cc. $CaCl_2$ (10 m.e. CaO per liter)
B. 20 cc. Na_2HPO_4 (2.42 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	Flocculation		μ/sec. 1 volt/cm.	pH	P_2O_5 in supernatant liquid	P_2O_5 in precipitate
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.010	.....	Clear	xxxx	0.00	6.8	1.95	0.47
0.028	.....	Clear	xxxx	− slow	7.2	0.53	1.89
0.049	.....	Clear	xxxx	.....	8.2	0.10	2.32
0.059	.....	Slow	xxxx	− slow	9.0	0.06	2.36
0.069	.....	Rapid	xxxx	.....	10.0	0.03	2.39
0.197	.....	Rapid	xxxx	.....	11.0	0.03	2.39
0.492	.....	Rapid	xxxx	.....	>12.0	0.03	2.39

200 cc. $CaCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	CaO added	CaO in liquid	CaO in precipitate	P_2O_5 in liquid	P_2O_5 in precipitate	Mol. ratio $\frac{CaO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
6.8	56.0	42.5	13.5	13.6	10.59	3.20
9.0	56.0	35.1	20.9	0.1	24.1	2.20
12.0	56.0	23.6	32.4	Trace	24.2	3.40

is stable only around pH 10, and is very susceptible to both alkaline and acid hydrolysis, whereas calcium phosphate is more stable on the alkaline side but goes into solution at pH 6. Bassett (1), on the basis of some results obtained with calcium phosphate, suggested that in faintly alkaline solutions, the compound would have the structure $(Ca_3P_2O_8)_3\ Ca(OH)_2$, and Russell (18) suggests that calcium phosphate added to the soil would tend to be converted into this substance. The formula itself has no meaning, and since there is a large group of soils, the podzols, which have a pH considerably below that at which calcium phosphate can be formed, the formation of calcium phosphate is doubtful in most of them, the reversion taking place by combining with iron and aluminum.

TABLE 9

The $CaCl_2$ + Na_2HPO_4 system

A. 20 cc. $CaCl_2$ (10 m.e. CaO per liter)
B. 20 cc. Na_2HPO_4 (4.84 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	.....	Clear	Clear	.....	6.0	....	....
0.010	.....	Clear	xxxx	±0.00	6.6	2.90	1.94
0.020	.....	Slow	xxxx	±0.00	6.8	2.29	2.55
0.040	.....	Rapid	xxxx	− slow	7.1	1.64	3.20
0.098	.....	Rapid	xxxx	.....	10.2	0.75	4.19
0.246	.....	Rapid	xxxx	.....	>12.0	0.75	4.19
0.492	.....	Rapid	xxxx	.....	>12.0	Very low	4.84

200 cc. $CaCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	CaO ADDED	CaO IN LIQUID	CaO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{CaO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
6.6	56.0	37.30	18.7	28.3	20.1	2.37
7.6	56.0	14.20	41.8	10.8	37.6	2.82
12.0	56.0	3.78	52.2	Trace	48.4	2.75

TABLE 10

The $CaCl_2$ + Na_2HPO_4 system

A. 20 cc. $CaCl_2$ (10 m.e. per liter)
B. 20 cc. Na_2HPO_4 (9.68 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	.....	Clear	xxxx	−0.7	6.8	5.71	3.97
0.010	.....	Clear	xxxx	−0.7	6.8	5.55	4.13
0.020	.....	Slow	xxxx	−1.0	7.0	5.29	4.39
0.049	.....	Rapid	xxxx	−1.51	7.8	5.19	4.49
0.069	.....	Rapid	xxxx	.....	8.8	5.19	4.49
0.089	.....	Rapid	xxxx	.....	10.2	5.19	4.49
0.246	.....	Rapid	xxxx	.....	11.2	5.19	4.49
0.492	.....	Rapid	xxxx	.....	12.0	5.19	4.49

200 cc. $CaCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	CaO ADDED	CaO IN LIQUID	CaO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{CaO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
6.8	56.0	17.0	39.0	57.8	39.0	2.53
7.6	56.0	5.2	50.8	48.0	48.8	2.65
12.0	56.0	3.3	52.7	48.0	48.8	2.75

TABLE 11

The $MgCl_2$ + Na_2HPO_4 system

A. 20 cc. of $MgCl_2$ solution (10 m.e. MgO per liter)
B. 20 cc. of Na_2HPO_4 solution (2.42 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.049	.....	Clear	xxxx	−0.33	9.0	1.30	1.12
0.069	.....	Opal	xxxx	.....	10.0	0.38	2.04
0.079	.....	Slow	xxxx	−0.45	10.0	0.42	2.00
0.148	.....	Slow	xxxx	.....	10.2	0.42	2.00
0.246	.....	Slow	xxxx	.....	10.3	0.80	1.62
0.492	.....	Slow	xxxx	−1.51	>11.6	1.09	1.33

200 cc. $MgCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	MgO ADDED	MgO IN LIQUID	MgO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{MgO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
9.0	40.32	29.55	10.77	13.74	10.46	3.60
10.4	40.32	15.28	25.04	4.90	19.30	4.56
11.2	40.32	0.36	39.96	10.77	13.43	10.52

TABLE 12

The $MgCl_2$ + Na_2HPO_4 system

A. 20 cc. $MgCl_2$ (10 m.e. MgO per liter)
B. 20 cc. Na_2HPO_4 (4.84 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.059	.....	Very slow	xxxx	−0.76	7.8	3.16	1.68
0.074	.....	Slow	xxxx	−0.76	8.0	2.66	2.18
0.084	.....	Slow	xxxx	−1.00	8.2	2.66	2.18
0.118	.....	Slow	xxxx	−1.00	9.0	1.70	3.14
0.173	.....	Slow	xxxx	−2.02	10.4	1.56	3.28
0.246	.....	Slow	xxxx	.....	10.6	1.56	3.28
0.492	.....	Slow	xxxx	.....	>12.0	2.54	2.30

200 cc. $MgCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	MgO ADDED	MgO IN LIQUID	MgO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{MgO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
8.2	40.32	27.52	12.80	33.80	14.60	3.09
10.0	40.32	13.47	26.85	21.79	26.61	3.56
11.2	40.32	Trace	40.32	29.94	18.46	7.61

TABLE 13

The $MgCl_2$ + Na_2HPO_4 system

A. 20 cc. $MgCl_2$ (10 m.e. MgO per liter)
B. 20 cc. Na_2HPO_4 (9.68 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	Flocculation		μ/sec. 1 volt/cm.	pH	P_2O_5 in supernatant liquid	P_2O_5 in precipitate
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.025	.....	Clear	Clear	.....	7.74	....	....
0.050	.....	Slow	xxxx	−1.01	8.60	8.00	1.68
0.069	.....	Slow	xxxx	.....	9.20	7.31	2.37
0.089	.....	Slow	xxxx	−1.2	10.10	7.00	2.68
0.108	.....	Slow	xxxx	−1.5	10.20	6.37	3.31
0.173	.....	Slow	xxxx	−1.6	10.20	6.25	3.43
0.246	.....	Slow	xxxx	.....	10.80	6.25	3.43
0.492	.....	Slow	xxxx	.....	>12.0	6.67	3.01

200 cc. $MgCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	MgO added	MgO in liquid	MgO in precipitate	P_2O_5 in liquid	P_2O_5 in precipitate	Mol. ratio $\frac{MgO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
8.4	40.32	24.91	15.41	75.94	20.86	2.59
10.2	40.32	10.07	30.25	63.69	33.11	3.23
11.0	40.32	Trace	40.32	68.59	28.21	5.41

ELECTROKINETIC POTENTIALS[4]

The interpretation of electrokinetic potentials presents considerable difficulties, but a great deal of confusion has arisen by limiting the outlook to compounds whose chemical structure is unknown, and by confining the viewpoint almost completely to the derivation of mathematical equations for calculating the charge. This has caused the neglect of most physicochemical changes which have a material influence on the nature and degree of potential acquired by soil colloids, such as the pH of the medium, exchange reactions that occur at the surface of colloidal micelles, and the great influence of solubility within a certain pH range. Michaelis (15) has emphasized the analogy between ordinary electrolytes and a very large class of colloids, and the work of McBain on soap solutions served further to demonstrate the relationship between the two.

While the Na-salts of the lower fatty acids in water form pure binary electrolytes, those of the higher fatty acids assume more and more colloidal properties. Their anion component no longer forms free ions, but rather micelles of fatty acids, with a surface dissociation. The existence of such a large polyvalent anion brings about electrostatic effects, with an extremely

[4] This discussion is drawn from the account as given by Michaelis, but has been added to, in order to bring soils, silicates, and phosphates into the same group.

strong electrostatic field in the neighborhood of the anion, whereby the cations while remaining free to move amongst themselves are distributed unevenly and are arranged in the form of a diffuse layer surrounding the anion. Under the influence of an applied potential the anions move in one direction and the cations in the other. Electrolytic conduction on this viewpoint is considered as a limiting case of cataphoresis where because of the high degree of dispersion of the dissolved substance the ions on the whole move independently of each other.

In certain aspects there are, however, important differences between dissolved electrolytes and colloidal electrolytes. With dissolved electrolytes, because of the small size of the ions, their mechanical and electrical mobilities are very high, and also in the special case of soap solutions McBain found that the electrical mobility of soap micelles approached those of smaller anions. Arrhenius in his well-known theory of electrolytic dissociation assumed the existence of ions, the dissociation increasing with dilution, but he further assumed that the electrostatic attraction and repulsion between the ions could be neglected in comparison with the mass action effect that they would display if they acted as molecules. His theory worked well with weak electrolytes but failed with strong electrolytes and was later substituted by the theory of Debye and Hückel (6), who, taking interionic forces into account and assuming a dissociation of 100 per cent, overcame the difficulties represented by the anomaly of strong electrolytes. Colloidal electrolytes, however, represent an extreme case, for here the electrostatic attraction between the micelles and the simpler ions of opposite sign is so great that it entirely dominates all other phenomena. The difficulties in the application of the theories for soluble electrolytes to colloidal electrolytes are, however, enormous. Although the similarity between a large number of colloids and electrolytes is quite obvious from the work of McBain (12), Michaelis (15), Loeb (11), and Mattson (13), there is as yet no definite quantitative expression.

Whereas the conductivity of soaps is high, the conductivities of soils are so very low as to give them the appearance of not being colloidal electrolytes, but actually they are, although very weak ones. Although Debye and Hückel's (6) theory of 100 per cent dissociation works well for strong electrolytes, the fact still remains that the original theory of Arrhenius of fractional dissociation is adequate for the interpretation of the dissociation of weak organic acids such as acetic acid, but not with their salts, which are strong electrolytes. The original assumption of Arrhenius of the existence of undissociated molecules with weak acids is undoubtedly correct, for the peculiar position of the hydrogen ion enables it to form a co-valency with the lone pair of electrons of the oxygen which is all that it requires to achieve stability

$$\left[\mathrm{X{:}\ddot{\underset{\cdot\cdot}{O}}{:}H}\right] \rightleftarrows \left[\mathrm{X{:}\ddot{\underset{\cdot\cdot}{O}}{:}}\right]\mathrm{H}$$

and a weak acid at ordinary dilutions exists largely in the co-valent form. Cations other than the hydrion require a valence group of eight electrons for stability and with a bond of the above type are electrovalent salts (10).

The silicates, the phosphates, and the soil have, from their most probable method of formation, a hydroxyl group at the surface, and the saturation capacity increases with the pH of the leaching solution. This, as has previously been stated, can be interpreted only on the basis that the dissociation of the hydrion is a function of the pH, and ion exchange is a secondary reaction. Because of the ease of formation of a co-valency between the oxygen and the hydrion their dissociation is weak and their conductivity values are low, as compared with soaps.

The question of the value of the determination of the isoelectric point and in particular of its correlation with pH and the saturation capacity naturally arises. Colloids are divided by Michaelis (15) into acidoids, basoids, and ampholytoids. Among the acidoids are the soaps investigated by McBain, and in the case of soil colloids those of extremely high silica content can function as pure acids. Ampholytoids consist of a large class of substances such as proteins, hydroxides, and nearly all soil colloids. With soluble ampholytoids the equation correlating the hydrogen-ion concentration with the strength of the acidity or alkalinity developed is correlated with the isoelectric point by the expression

$$I = \sqrt{\frac{Ka}{Kb} \cdot Kw}$$

where I = hydrogen-ion concentration at the isoelectric point, Ka Kb the dissociation constants for the acidoid and basoid components, Kw the dissociation constant for water. When the cationic and anionic dissociations are equal the isoelectric point is reached and the dissociation is at a minimum, but may vary enormously in degree from colloid to colloid.

It has previously been shown that the adsorption of anions from a salt solution by colloidal hydroxides (16) bears a distinct relationship to the exchange acidity or alkalinity developed, exchange alkalinity being developed if the colloid is treated with a salt solution, the pH of which was originally below the isoelectric pH of the colloid, and exchange acidity if the pH of the salt solution was originally above the isoelectric pH of the colloid, and the same reaction was found by Mattson and Hester to hold for a large number of compounds. During the formation of these phosphates by the substitution of chlorine by hydroxyl and phosphoric acid groups, sodium chloride is of course formed, and exchange of chlorine for hydroxyl and of sodium for the hydrogen ions can take place, depending on the pH of the salt solution and the isoelectric pH of the colloid. At a low pH when the colloid dissociates hydroxyl ions, the dissociation is suppressed by increasing the pH, and with a solution of high pH when the colloid dissociates hydrions the dissociation of these is suppressed by lowering the pH, and there is a consequent decrease in the electrokinetic potential.

Although the interpretation of electrokinetic potentials is thus complicated, the determination of the isoelectric point gives results of great practical value

for the determination of ion exchange. With the hydroxides (16) no base exchange is possible if the colloidal hydroxides are leached with a solution the pH of which is equal to the isoelectric pH. With other compounds there is base exchange at the isoelectric pH, but it becomes smaller at a pH below the isoelectric pH and increases rapidly above. In a previous paper (16), in order to interpret this remarkable property, it was assumed that the isoelectric point is that point at which the amphoteric colloid has a mininum of the electrovalent form, with hydrions and hydroxyl ions dissociated in an equal degree.

This general review of electrokinetic potentials applies to all the phosphates. Tin hydroxide was found to be isoelectric at pH 3.9, but the substitution of a hydroxyl by a phosphoric acid group increases its acidoid component, and it becomes electronegative at all points of the pH range at which it is precipitated. Calcium and magnesium phosphates are also electronegative at the pH range at which they are precipitated and are within this range functioning as acidoids, for their solubility at a lower pH is so high that they cannot be precipitated in the electropositive condition.

SUMMARY

A series of phosphate precipitates of tin, titanium, iron, aluminum, calcium, and magnesium were prepared, and their cataphoretic behavior and phosphate content at different pH were determined.

Tin and titanium have strong acidic properties and only weakly adsorb phosphoric acid. The compounds, however, are very insoluble and stable in acid solutions, but are dispersed when the pH is increased to about pH 6.0. The phosphates of ferric iron and aluminum are of the same type, but ferric phosphate is more stable in the very acid ranges than is aluminum phosphate. Calcium phosphate is insoluble within a pH range from neutral to strongly alkaline. Magnesium phosphate is less stable than calcium phosphate and more susceptible to both acid and alkaline hydrolysis.

By increasing the pH the phosphate content of the precipitates of tin, titanium, iron, and aluminum is diminished, the hydroxyl replacing the phosphoric acid. Two effects are, however, apparent: the replacement of the phosphoric acid by the hydroxyl groups, and the necessity of having a certain degree of pH in order to obtain the requisite degree of polymerization of the molecules and prevent both acid and alkaline hydrolysis. Since only the pH has been determined in this case, there is no means of deciding the number of hydroxyl groups required to replace the phosphoric acid. On the theory of coördination, however, and in the absence of double bonds, only one hydroxyl group would be required to replace a large group like H_2PO_4 or $HSiO_2$. Definite evidence for this will be published later, as it gives us a means of determining the structure of the internal core in phosphates and silicates.

The significance of electrokinetic potentials and the isoelectric point is discussed.

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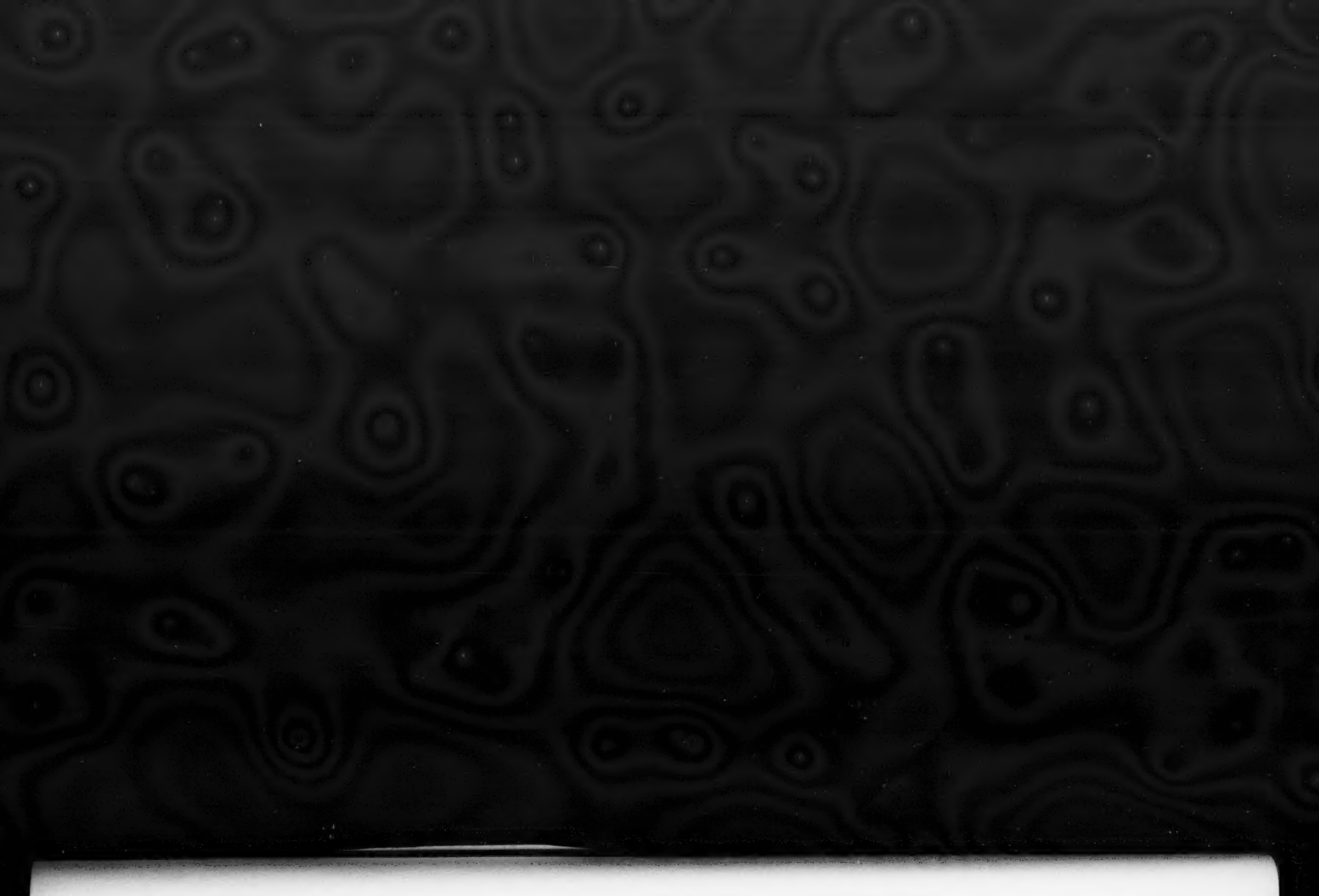
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